AN EVALUATION OF PHOTODEGRADATION INHIBITORS IN THE CONSERVATION OF NATURALLY DYED HISTORIC SILKS

VOL. I

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by

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To my parents

Στους γονείς μου

Abstract

Photodegradation of naturally dyed historic silks is a problem that confronts many museums. It continues as long as the objects are displayed, as both ultraviolet and visible light are capable of causing degradation. Degradation may be seen in the fading of the dyes and in the loss of textile strength.

Five photodegradation inhibitors were tested on silk dyed with natural red dyes and dye combinations in order to evaluate their ability to increase the light fastness. The selected additives belong to the classes of UV absorbers and antioxidants, and combinations of those were also tested in order to investigate a possible synergetic effect.

The preparation of sampling material was based on original silk samples taken from Greek museums and identified in detail using scanning electron microscopy (SEM), energy dispersive X-ray analysis and high performance liquid chromatography. Evaluation was focused on the colour induced changes after artificial ageing of the treated samples and also on the tensile strength, the application methods, and the prospective reversibility of the additives.

Exposure to electromagnetic radiation was performed with British Standard method BS1006:1990 using blue wool standards, by gradually covering the samples in order to investigate the fading rates over specified time periods, with an increase of temperature to 50°C and in three different relative humidity levels of 30%RH, 50%RH and 80%RH keeping stable temperature at 35°C. Colourimetric measurements were used for the evaluation of colour changes using the system of the Commission International de l' Éclairage (CIE). Comprehensive SEM investigation was performed on the inhibitor-treated samples.

Benzophenone and hindered amine types showed promising results on individual samples, but an inhibitor combination of an ultraviolet absorber and an antioxidant showed good performance over a wide range of dyes and dye combinations. Synergism was confirmed in two inhibitor combinations which improved light fastness at all three humidity levels, with the best performance shown at the lowest humidity. In every case, the inhibitors proved more effective on the more light stable dyes such as madder and cochineal, while less photoprotection was given to the more sensitive dyestuffs such as brazilwood and safflower. Consideration was also given to the ethics of using photodegradation inhibitors in historic textiles.

The research has shown that the use of the selected photodegradation inhibitors is not recommended on historic silks according to the present conservation requirements and codes of practice.

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Preface

Light is a major cause of degradation in historic museum textiles, and its action is referred to as photodegradation or photodeterioration. The terms describe the deterioration initiated by any form of light energy, which causes the textile's dyes to fade and its fibres to weaken. Photodegradation of textile materials is continuous, from the day of manufacture throughout their use, and during museum display. Textiles can be protected only if they are kept in complete darkness. Photodegradation is non-reversible and conservation science has been focusing for many years on the retardation of further deterioration by preventive conservation methods, and on addressing the outcome of photodegradation by remedial conservation practices. The subject of the present research is the evaluation of an interventive but also preventive conservation treatment for the improvement of lightfastness on historic textiles, following some successful industrial applications.

The sun emits radiation of all wavelengths, whereas artificial light sources selectively emit radiation from different parts of the spectrum. Ultraviolet (UV) radiation is responsible for the largest part of photodeterioration of polymer materials, because of its short wavelengths with high energy *(see section 1.1).*

Natural fibres and dyes are naturally occurring polymers, which have the tendency to absorb electromagnetic radiation *(see sections 1.2 and 1.3).* As the absorbed energy may be sufficient to break chemical bonds in the polymer molecule, fibres and dyes can easily undergo degradation caused by photochemical reactions. This can result in changes in the mechanical properties and discolouration of the fibres as well as the fading of the dyes *(see*

section 2.1). Knowing the above, the noticeable fading and deterioration of curtains, tents, automobile upholstery and outdoor furniture, in a very short period of time, is not surprising.

As far as modern fabrics are concerned the problem is confronted by simple replacement after some time. Moreover, modern manufacturing processes have developed new fabrics enriched with additives that appear to have high light stability, maintaining their physical properties and appearance for long periods, though not forever. The case is not the same with historic textiles, which need to be kept in good condition for as long as possible, in order to preserve their authenticity and their physical appearance.

When objects become part of a museum collection, it is necessary to develop methods to protect them from further photodegradation. During storage, it is easy to keep objects in darkness. However, textiles which are exhibited in display cases or even in the open environment of a museum, are prone to photodegradation. Modern museums use several methods to face the problem such as exclusion of natural light, controlled artificial light, UV filtering on light sources, and specially manufactured cases with controlled environmental conditions *(see section 2.2).* However the problem still exists, as any kind of lighting, even controlled, causes deterioration.

There are instances such as historic buildings, open houses, folk art collections and palaces, from which natural sunlight cannot be excluded, as it is part of the visitor's experience. Similarly, when exhibitions are moved to different galleries and museums, historic textiles are exposed to non-ideal conditions. Finally, the installation of sophisticated lighting systems and environmental control units are expensive solutions and are applicable only for large and well funded museums.

A comprehensive study of the literature of modern polymer industry, presented in *Chapter 4,* revealed the extensive use of additives, known as *photodegradation inhibitors*, which improve significantly the light fastness of several organic polymers, among them natural

fibres and dyes. Their photo-stabilization mechanisms are based either on the blocking of ultraviolet light, which is considered the most destructive, or the elimination of photo-oxidation reactions *(see section 4.3).* Finally, mixtures of these additives proved to present a synergetic effect giving better stabilization results to polymers on which they were applied *(see section 4.4).* The purpose of the present research is to examine the potential of these materials for historic textiles, based on some successful former applications but customized on conservation needs, restrictions and ethics and the complexity of historic textiles.

In the conservation field, photodegradation inhibitors have been evaluated as additives in picture varnishes, protective coatings and adhesives with some promising results *(see section 4.2.)*, but there is no comprehensive research in historic textile conservation, although some testing with natural fibres and dyes has been reported *(see section 4.1.b).*

What was clear from the beginning of this research was the need to evaluate additives that had been successful in modern polymer industry, according to conservation requirements. These requirements are different from other applications due to the complex needs of historic textiles and this was the main scope of this study.

The experimental procedure was based on original historic textile samples subject to photodegradation, dyed with natural dye mixtures, a phenomenon usually observed in historic textiles *(see chapter 7).* The application method follows acceptable conservation procedures, and the evaluation of treatments was done with regard to conservation requirements: accelerated ageing tests were based on museum conditions, the removability of the additives after aging was considered *(see chapter 9),* and conservation challenges and ethics were taken into account *(see chapter11).*

The results showed the potential of these materials for the photo-protection of historic textiles, and the scope for further research. For example, an inhibitor combination increased the light stability of some samples by up to 40%. On the other hand, many conservation

questions are raised, such as the consistency of the results and the long term effects of the treatments. The present study therefore is considered an introduction to a prospective conservation treatment, dealing with some selected parameters in order to address the complexity of the subject, whilst giving special attention to the conservation standpoint.

1. Background: Light, the silk fibre and natural dyes

In this chapter the action of light on organic polymeric materials is discussed and basic information is given on the silk fibre and natural dyes used on historic textiles relevant to their susceptibility in photodegradation. This information is chosen according to the final choices made on this research, in order to give the reader the basic background on photodegradation mechanisms *(see chapter 2)* and how these can be inhibited with the action of additives *(see chapter 4)*.

1.1 Light and its properties

The sunlight that reaches the earth consists of a continuous spectrum of radiant energy. The sun emits radiation of all wavelengths, from Gamma-rays [0,03 – (3×10^{-4})nm] to Power region [(3×10^{8})-(3×10^{5})m] but the earth's atmosphere is almost completely opaque to radiation below 300nm (Brill 1980, 8) (*see Figure 1*).

Most regions of electromagnetic radiation have many and important applications, but as far as art and historical materials are concerned the most important regions are infrared, visible and ultraviolet, because historical objects are exposed regularly to these radiations during use and display.

Of all the sun's radiation, reaching the earth's surface, the largest proportion (about 45%) lies between 400-700nm and is visible to the human eye, as visible white light. Visible radiation is generally divided into six intervals according to the wavelengths from the longest to the shortest between the visible range, red, orange, yellow, green, blue and violet, based on the theory of colour by Isaac Newton in 1672. The response of the human eye to different wavelengths in the

visible region gives us the consciousness we understand as colour, texture, transparency, etc. (Brill 1980, 11) *(see also 1.3).*

Radiation between 10^5 - 700nm is invisible to the human eye and constitutes the infrared region of the spectrum. It is also referred to as radiant heat as the rays contained in this region have a tendency to increase the temperature of whatever they irradiate. The heating effects of infrared radiation are the most important feature of this region as they are capable of mechanical and chemical changes on materials, although chemical reactions are usually a secondary effect of the infrared radiation. This is because of the heat produced by infrared exposure which accelerates most chemical reactions.

Figure 1. The electromagnetic spectrum

*Data taken from Keiner 2006 (http://en.wikipedia.org/wiki/Image:Electromagnetic-Spectrum.png)

The shorter wavelengths of the solar spectrum, between 10-400nm are also invisible to the human eye, and are termed ultraviolet light (UV). This region can be subdivided into four smaller regions, the vacuum ultraviolet (10-180nm), the far-ultraviolet (180-280nm), the middle-ultraviolet (280-300nm) which causes skin tanning, and the near-ultraviolet (300-400nm).

Ultraviolet light, which represents only a small portion of the sun's electromagnetic radiation, is believed to be destructive to many organic materials (Coleman and Reacock, 1958, Brill, 1980, Mills and White, 1987, Nicholson, 1991, Feller, 1994, Timar-Balazsy and Eastop, 1998). In fact, ultraviolet radiation with wavelengths reaching the earth's surface in the range of 300-400nm, is responsible for most photochemical reactions including bond rupture in many organic materials (Brill 1980, 10).

Summarizing the above in Table 1, one can see the events that occur in molecules when exposed to electromagnetic radiation emitted by the sun.

*Table 1.Molecular events induced by various wavelengths of radiation**

*Table data taken from Brill 1980, 8

The most important source of light is of course the direct sunlight and the energy distribution of it is dependent on many parameters such as the time of the day, the season, the altitude, the latitude and several atmospheric conditions. As the sunlight radiation reaches the earth's atmosphere, wavelengths below 150nm are absorbed by the photochemical ionization of nitrogen and oxygen atoms at an altitude above 50km. The radiation between 150-290nm is absorbed by the ozone layer of the atmosphere at an altitude of 20-30km, while the rest of the light with wavelengths between 300-5000nm is able to reach the earth's surface (*see Figure 2)* (Encyclopedia of pol.sc.tech. 1971, Garisson and Wiles 1975).

Figure 2. Atmospheric electromagnetic transmittance or opacity

*data taken from NASA 2007,

(http://en.wikipedia.org/wiki/Image:Atmospheric_electromagnetic_transmittance_or_opacity.jpg)

The concentration of ozone layer is very small and it is distributed in the stratosphere (90%) and the troposphere (10%). If all of the ozone were compressed to the pressure of the air at sea level, it would be only a few millimetres thick. The thickness of the ozone layer in the atmosphere varies according to the season and latitude. For example, it is higher in the winter time and lower in the summer months, whereas it is thinnest in the equator where it shows no seasonal variation (Barker 1968). Consequently the sunlight exposure during summer months is much more dangerous[1] and it has been proven to be five to ten times more severe than during the winter months. Furthermore other factors, such as smoke, dust, air pollution and sulfur dioxide cause local variations in the intensity of the solar ultraviolet light (Encyclopedia of pol.sc.tech. 1971). It has also been suggested that the variation of the concentration of the ozone layer may

[1] Being very energetic, UV can break chemical bonds, making molecules unusually reactive or ionizing them, in general changing their mutual behaviour. Sunburn, for example, is caused by the disruptive effects of UV radiation on skin cells, which can even cause skin cancer, if the radiation damages the complex DNA molecules in the cells

reduce the atmospheric cutoff to 270nm or less, and this sort of ultraviolet rays (middle-ultraviolet region) are primarily responsible for polymer photodegradation (Barker 1968).

1.1.a Light and degradation of polymers

Light consists of photons (bundles of energy) that pose wave characteristics. The photons with the shortest wavelengths have higher energy and are found in the ultraviolet region of the spectrum. When a molecule of a polymer material absorbs light, the energy of the absorbed photon is conveyed to the absorbing molecule. If the amount of energy absorbed by the molecule is greater than the energy of the bonds present in its chain, these bonds will be broken, and the polymer damaged (Brill, 1980, Mills and White, 1987, Nicholson, 1991, Feller, 1994, Timar-Balazsy and Eastop, 1998).

Such breaking of polymer chains is termed as photodegradation and can be explained in the following way. Polymers have some light-absorbing groups of molecules, which absorb photons from light radiation; these groups are then raised to a higher energy level, referred to as an excited state. The polymer molecule can discard the excitation energy in several ways without damaging the molecule. For instance, by releasing energy as heat or by re-emitting light in the way of fluorescence or phosphorescence. However, some energy may be kept in the molecule, and cause degradation. The excited molecules may lose the absorbed energy by undergoing a chemical change within the molecule and/or by the breaking of chemical bonds or by transfer of the energy to another atom or molecule (Feller 1994, 49). Although the number of excited molecules undergoing degradation is very small, solar ultraviolet light is capable of breaking quite a significant number of molecular bonds over the course of a year's exposure, enough to be considered as degradation.

The quantity of the light absorbed by a polymer either in ultraviolet or visible region, the quantum efficiency of its degradation[2] and the chemical reactions that occur during photodegradation depend on the polymer's molecular structure and are therefore different for every polymer (Bowen 1946, 193).

Usually as far as art objects are concerned (paints, varnishes, textiles, etc.), the quantum efficiency is much lower than 1 and thousands of photons are needed to be absorbed in order to photodegrade for example two dye molecules. If the intensity of illumination is lowered, the number of photons per minute is diminished and therefore the process of photochemical deterioration will be delayed, but this does not mean that the energy of the absorbed photons will be reduced as this depends on their wavelength. This leads us to the conclusion that *there is no level of intensity of light below which no photochemical reaction can occur* (Feller 1994, 50).

1.1.b. The reciprocity law

In order to eliminate photodegradation it is essential to reduce both illumination rates and exposure times according to the reciprocity law (Thomson 1986, 21) which states that the cumulative photochemical effect is proportional to the product of intensity and time (Carver 1994, 74). This means that any kind of radiation, even it is high or lower energy will act collectively on the irradiated object so what is of importance is the total dose of radiation absorbed by the material (Thomson 1986, 21).

Photodegradation caused in a textile object therefore is cumulative with the passing of time, but the rate of fading is not constant, as it has the tendency to decrease until no further fading can occur. From the above can be understood that the rate of fading is not proportional to the dose of irradiation and of course it will be different for each material.

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[2] Quantum efficiency (Φ) of degradation = the ratio of the number of molecules undergoing degradation to the number of quanta absorbed. "If one molecule is changed or decomposed for every photon of light absorbed, the quantum yeld of quantum efficieny is equal to 1, as predicted by the Stark-Enstein Law" (Feller 1994, 50).

1.2 The silk fibre

The silk fibre is a naturally occurring polymer. While synthetic polymers can be manufactured in a short period of time, natural polymers usually need weeks, months and even years to be produced by animals or plants and require specific atmospheric conditions. The transformation of chemical monomers into polymers occurs inside plants or animals and polymerization requires enzymes and enough energy to help cell response and growth (Hatch, 1993).

Silk's receptiveness to dyeing with natural dyes gives bright and shiny colours, which is an advantage against other fibres, especially in association with the red dyes which have given silk a royal identity. The orange madder red, the safflower pink and the cochineal red are some of the shades commonly used in cultivated silk fibres in different cultures around the world like Asia and along the Silk Road, the Ancient World, Egypt , the Byzantium and later European civilizations (Scott, 1993).

It is no surprise therefore, that silk textiles can be found in historic textile collections in museums all over the world. The problem that all such institutions are facing is the protection of historic silks from light. Silk is considered to be the most susceptible fibre to photodegradation (*see*: Becker et al, 1989, Harris, 1984, Timar-Balazsy and Eastop, 1998) *(for more details on photodegradation of silk fibres see 2.1.b).*

Silk is a natural protein fibre excreted by the moth larva *Bombyx mori*, commonly known as silkworm. It is the only natural continuous filament fibre of high gloss and strength and it is a highly prestigious fibre. It may be up to 600 meters in length but it is usually around half this size. It has a fine diameter of 12-30 μm that is dependent on the health and diet of the silkworm that produced the filament. There are other types of silk fibres like the *Tussah silk*, also called wild silk. The silk taken directly from the cocoon of any type consists of two silk filaments stuck and

coated together with sericin[3], which is later dissolved and removed leaving two filaments of uneven diameter along their length (Needles, 1981,Hatch, 1993,Gohl and Vilensky, 1983).

Silk falls in the category of protein polymers (polypeptides) and is synthesized from amino acids monomer units. The silk protein is called fibroin and is composed of 15-16 different amino acids depending on the type of silk fibre. The amino acids composing the silk protein are summarized in the following Table 2 (Gohl 1983). As can be noticed, only three of them (glycine, alanine and serine) make up about 86% of the fibroin. The silk fibroin is much simpler in structure than other keratin fibres (like wool and hair) and contains fewer amino acids in its composition[4]. With no cystine[5] present in the fibroin protein, there is little cross-linking between protein chains.

The degree of polymerization of silk protein is unpredictable. The fibroin molecules arrange themselves parallel to each other as there are no cross-links or large side chains in the amino acids. The chains lie close together and form numerous hydrogen bonds which form a highly crystalline "beta" structure *(see Figure 3).*

Figure 3. Beta configuration of silk

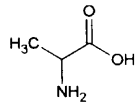
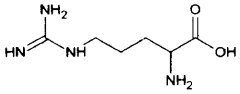
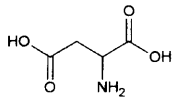
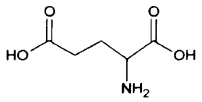
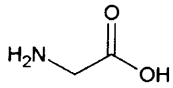
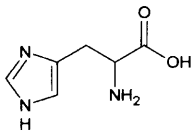
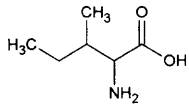
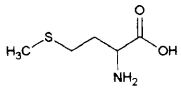
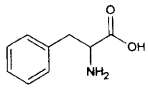
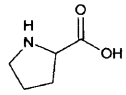
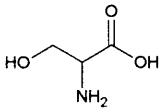
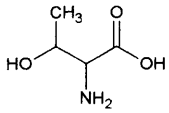
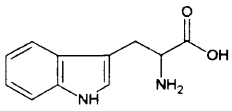
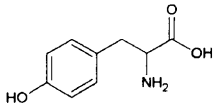
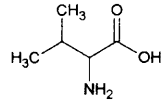
*data taken from A. Timar-Balazsy, D. Eastop 1998

[3] also called gum or silk glue

[4] Wool consist of 18 amino acids

[5] Cystine: amino acid present in the wool protein (-CH_2SSCH_2-)

Table 2. Percentage of amino acids in silk (data taken from E.P.G. Gohl, L.D. Vilensky, 1983)

Amino acids	Amino acid content (%)
Alanine 	26.54
Arginine 	1.71
Aspartic acid 	1.29
Glutamic acid 	0.97
Glycine 	43.99
Histidine 	0.5
Iso-leucine 	0.64
Methionine 	0.58
Phenylalanine 	0.89
Proline 	0.4
Serine 	11.41
Threonine 	0.9
Thryptophan 	0.29
Tyrosine 	5.35
Valine 	2.1
Unidentified residues containing nitrogen	1.91

In the beta configuration of silk polymer chain the "R" side groups are very small and they require only a small amount of space in the stereochemical pattern of the molecule and the protein chains can be fully extended. This narrow pattern helps the formation of an important amount of secondary bonds between the chains. The chains in the fibroin of silk are held together by strong hydrogen secondary bonds (Needles 1984, 18-24).

Silk may be considered to have the same composition as wool but an important difference between them is that silk contains no disulfide bonds, as there are no amino acids containing sulfur in its synthesis. The important chemical groupings on silk are the peptide groups and carboxyl and amine groups.

The peptide groups contain the peptide bond or link which is shown as –CO-NH- as can be seen below *(see Figure 4).* The carbonyl oxygen of the peptide group is heavily electronegative. As a result it develops a small negative charge and gives rise to hydrogen bonds that occur between the carbonyl oxygen and hydrogen atoms of the silk polymer.

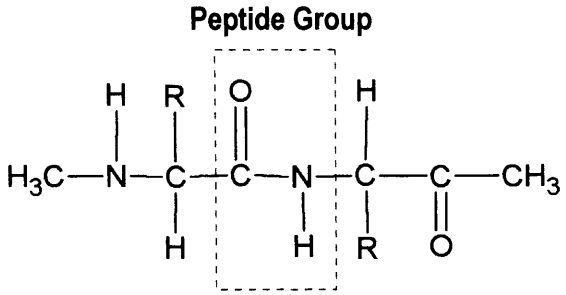


Figure 4. Peptide bond or link

Some silk polymers have carboxyl groups ($-COO^-$) as side groups while others have amino groups ($-NH_3+$) as side groups. Ionic bonds are formed between these two groups (Gohl and Vilensky, 1983).

1.3 Natural Dyes and the theory of dyeing

1.3.a Dyes and the causes of colour

The colouration of textile fibres dates back to prehistory in all cultural groups and on all major landmasses. For example, the practice of burying the dead on red ochre mantles in some cultures, goes as far back in time as the Old Stone Age (30,000 B.C) (Chenciner, 2000, 29). It is not known when exactly the dyeing of textiles, skins and basketry begun, and what the first dyes were, but the practice must have started quite early. The first colours used for textiles were probably more like stains, iron rust for yellow and orange, or iron tannate for grey and black. These kind of stable dyes were still in use until the beginning of twentieth century. But it is known that *turmeric, saffron*, and *annatto* were used quite early to dye fibres yellow as well as *safflower* for pinks and rose pink colours, since these dyes can be applied directly into the fibres without any pre-treatment other than washing (Direct dyes, *see section 1.3.c*) (Liles 1990).

It is important to notice the difference between dyes and pigments which are also colouring agents. Dyes are absorbed by the substrate and are dispersed throughout the material, whereas pigments form a coloured film, held on the surface with the use of a binding media. Pigments are usually inorganic materials, but all dyestuffs are organic compounds.

The final colour of the dyed fibres is subject to a number of parameters and can be understood, along with colour change during ageing, with the use of colour physics. Light coming from the sun appears white to the human eye because it contains all wavelengths *(see section 1.1)*. Every material absorbs light selectively (that is, only of certain wavelengths) resulting in the reflected complementary beam that reaches the eye, to appear coloured. It is understood then, that *colour is due to the selective absorption of visible electromagnetic radiation.*

When a dye absorbs electromagnetic radiation from the visible spectrum, some electrons in the molecules of the dye undergo a transition from their ground state to a higher energy level, a so called "excited state". An important property of a good dye is that these electrons quickly

return to their unexcited state and are then again able to absorb certain wavelengths of the visible spectrum. This is essential for the retention of the colour. In a different situation, the absorption of radiation would last only as long as it would take for all the electrons to be promoted to an excited stage, and then the colour of the material would disappear (Brill, 1980, 64).

Dye molecules become coloured and hence useful for dyeing because they contain the radicals *chromophores* and *auxochromes*. The chromophores[6] are responsible for the colour of the dye as they absorb and reflect incident electromagnetic radiation within a very confined band of visible light. The auxochromes[7] are responsible for the hue of the final colour, the solubility of the dye in water and the colour-fastness.

Dyes are usually introduced into the interior of a fibre by a water solution, known as a dyebath and are retained in the amorphous areas, within the fibres. The auxochromes appear to be the fundamental factor in the dyeing process as they increase the polarity of the dye molecules and make the dye more soluble in water. This assists the preparation of dyebaths and the uniform solution-uptake by the fibre. They also help in the formation of forces of attraction between the fibre polymer and the dye molecule (Mills, 1987).

The presence of polar auxochromic groups within the dye molecules is essential, as these groups make the dyestuff water-soluble and suitable for dying textile fibres. There are some organic compounds without auxochromic groups, which appear to be coloured and are insoluble in water. An example of this is *indigo* (Vat dyes, *see section 1.3.c*)

The main aim of the dyeing process is the bonding of the dye molecule to the fibre by secondary bonds and ionic bonds. Secondary bonds can build up between the dye and the fibre when the appropriate groups within the two are close to each other. In order to help the dye molecules to intrude easier into the fibre the temperature is raised. Hot water and the presence of

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[6] The name comes from the Greek *chroma*=colour and *phore* from *pherein* =to bear

[7] The name comes from the Greek word *auxein*= to increase and *chroma*= colour

surface-active agents and other additives help the swelling of the fibres during the dyeing process, and thus facilitate the diffusion of the dyestuff.

1.3.b Natural Dyes

Natural dyes are extracted from plants and animals. They are present in the majority of historic textiles as the introduction of synthetic dyes in the textile industry did not take place until 1856 (Hatch, 1993). Until then, all dyes came from flowers, fruits, roots, insects and shellfish and it was practically impossible for two of them to have the same colour, shade or fastness.

Natural dyes are derived from a number of plants and living organisms and they can be divided into two major classes: vegetable and animal dyes.

Vegetable dyes were extracted from different plants and the most common are madder, woad, indigo, weld, saffron, safflower, henna, sandalwood, brazilwood, annato, walnut, fustic, berries, oak and logwood. Extracting the dyestuff from the plant of origin usually involves boiling the leaves, flowers, berries, roots or bark of the plant in water. Dyes which are insoluble in water, like indigo, are extracted by a vatting process. During this process, an alkaline reduction takes place by effervescence in alkaline conditions which makes the dye water soluble. The dyestuff returns to its original form with oxidation by exposure of the dyed fibres in air.

Animal Dyes comes from the isolation of some mollusks, such as Tyrian purple, and some special insect bodies such as cochineal and kermes.

1.3.c Classification of dyes

Usually dyestuffs are classified according either to the way of application or their chemical structure.

Classes of dyes according the method of application

Direct dyes are applied to fibres by hot water solutions and are bonded to them by secondary bonds. Usually some electrolytes are added to the dyebaths to stop the repression between polar

groups of the fibre and the dye of similar polarity and to swell the fibres. Direct dyes are more suitable for cellulosic fibres (Ponting, 1980, 49) but were also used on wool and silk.

Acid Dyes is a class of dyes more suitable for protein fibres like wool and silk. During the dyeing process, acids are added to the dyebath. This is essential to protonate[8] the amino groups of the protein fibres. The dye molecule ionizes to form an anion in water which is negatively charged and bonds easily by ionic bonds to protonated amino groups which are positive. Additionally secondary bonds are formed between the dye and the fibre polymer. Most of the natural dyes, vegetable and animal, can be applied as acid dyes.

Basic Dyes are used mostly for protein fibres as they ionize in water to cations which show affinity to the carboxyl groups of the protein fibres. During the dyeing process ionic bonds are formed between the dye and the fibre. There is only one natural dye that can be applied as a basic dye, and that is *berberine* (Schweppe, 1987).

Mordant Dyes are those dyes that may belong to the direct or acid class, but contain auxochromic groups that form complex compounds with some metal ions. For that reason, the fabric has to be immersed in an aqueous solution of a metal salt, known as mordant, usually before the dyeing process or, sometimes, during or after dyeing. Mordants include metal oxides, tannins and oxyfatty acids (Liles 1990, 4). Mordant dyes are fast to washing because of the strong bonds formed between the dye and fibres by the metal ion and the formation of large and complex molecules.

An important characteristic of applying mordants to dyeing, is that the colour obtained from one single dyestuff can be changed with the variation of mordants. Many traditional dyestuffs are characterized as *polychromic* because several colours or shades can be obtained with the use of different mordants. Excellent examples of that are madder and cochineal (Liles 1990, 4) *(more information for these dyes in section 1.3.d).*

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[8] protonate: add protons to a heavy atom protein

Most of the natural dyestuffs are mordant dyes. The most widely used mordants in historic textiles are salts of aluminium, iron, copper, and tin but since the discovery of chrome as a mordant in the twentieth century and its extensive use thereafter, mordant dyes are frequently called chrome dyes (Ponting, 1980, 143).

Vat Dyes are not soluble in water and contain an insufficient amount of auxochromic groups. However, hydrophilic groups in the molecule can be formed by an alkaline reduction. In this way the dye becomes water-soluble and this is the so called *leuco* form of the vat dye. The dye is then absorbed by the fibre and when this is exposed to air the dye oxidises back to its normal non soluble form (Horsfall and Laurie, 1946, 85). One of the most common natural vat dyes is indigo, the leuco form of which is yellow with the blue colour returning upon oxidation.

Because there are no auxochromic groups within the dye molecule, vat dyes bond to fibres by Van der Waals and dipole bonds. They have a relatively good wash fastness because of their non-solubility in water, but they appear to have poor wear resistance.

Classes of dyes according to their chemical structure

Anthraquinone Dyes is the most important class as most of the natural dyes belong to this group. The main components of these dyes are alizarin, purpurin, pseudopurpurin, rudiadin, munjistin and alizarin β-methyl ether *(see Figure 5).* All of these can be found in madder, one of the most important natural dyes. The first three of these components give the red colour on madder dyeings while rudiadin, munjistin and alizarin β-methyl ether give orange with aluminium mordant[9].

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[9] Aluminium mordant (alum): Potassium aluminium sulphate $KAl(SO_4)_2 \cdot 12H_2O$ (Adrosco 1971, 118)
Strictly speaking, an alum is a double salt with the ground formula MAl $(SO_4)_2.12H_20$, in which M is a univalent cation. In practice, the term is often used to refer to aluminum sulphate.

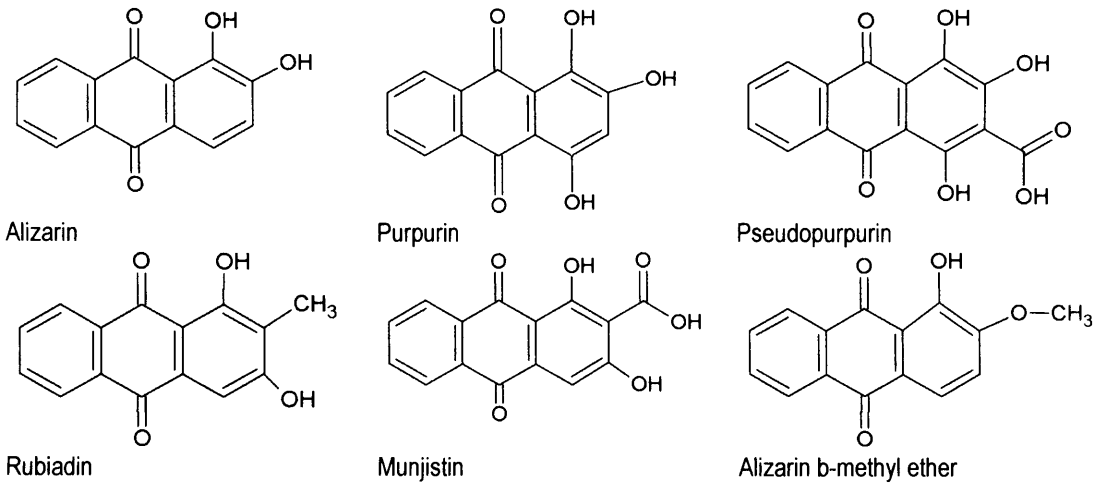

Figure 5. Main components of anthraquinone dyes

There are also animal dyes containing colouring compounds that belong to the class of anthraquinones. These are kermes, cochineal and lac. These insect dyes give red colours, from vivid pinks to reds and bluish violet, especially with the use of aluminum mordant. Other mordants have also been used with insect dyes like tin salts, giving bright red colours. The main coloured components of these dyes are kermesic acid, carminic acid and laccaic acid A *(see Figure 6)*.

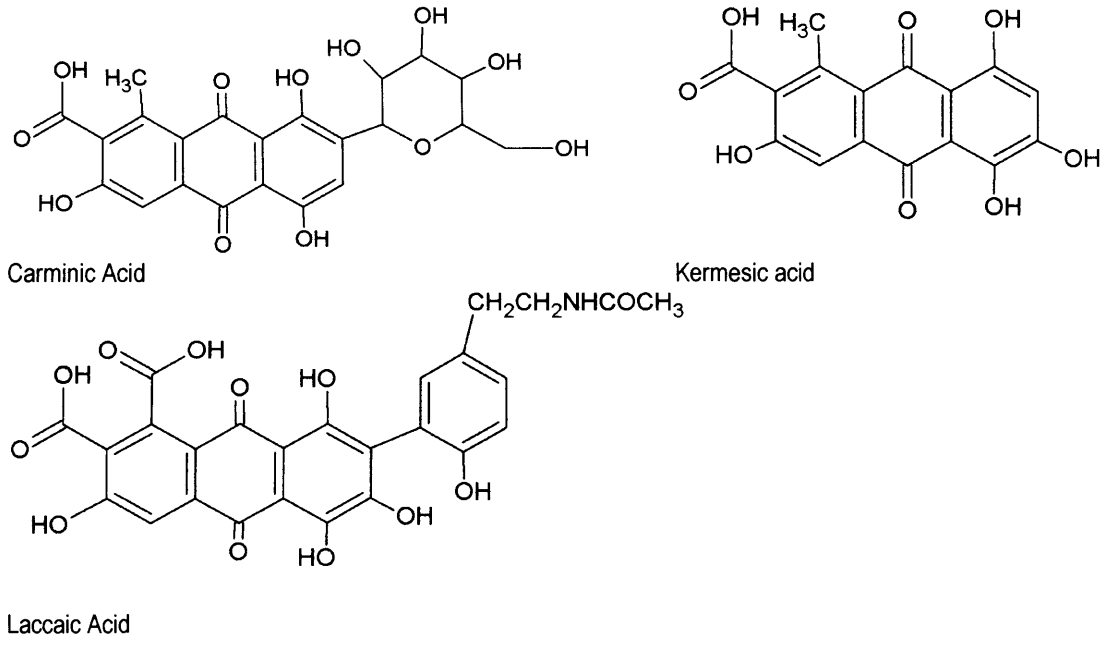

Figure 6. Main components of animal anthraquinone dyes

Flavonoid dyes are natural vegetable dyes and the most important of them are weld and fustic. The main compound of this group is flavonol. Flavonoid dyes are mordant dyes and they give various colours from yellow to greenish yellow and brown.

Quinoidic dyes have as a basic structure the naphthoquinone with the addition of various substitutes.

The most important natural dyes belonging to this group are alkanet, henna (*see Figure 7)* and black walnut. These dyes can be applied as acid, direct or mordant dyes and their colour is pink, orange, red, brown and black.

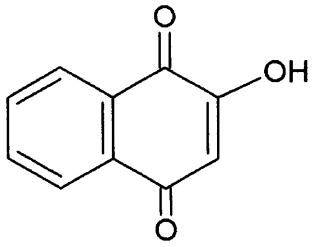

Figure 7. Lowsone (henna)

Carotinoid dyes include saffron and annato, two very important natural dyes. Saffron has excellent dyeing properties, a yellow colour and is used for dyeing wool and silk (Hogenk-De Graaf, 1969, 46).

Chalcone dyes are represented by safflower among the natural dyes. Safflower is one of the most ancient natural dyes because it can be applied as a direct dye and gives a beautiful pink colour. The main compound in safflower dye is carthamin which oxidizes to red carthamon *(see Figure 8).* The florets of safflower also produce a water-soluble yellow dye which is usually rinsed away.

Indigoid dyes are those containing indigotin, and are vat dyes. Woad has always been the most important indigoid dye and the indigo plant is the main source of indigo.

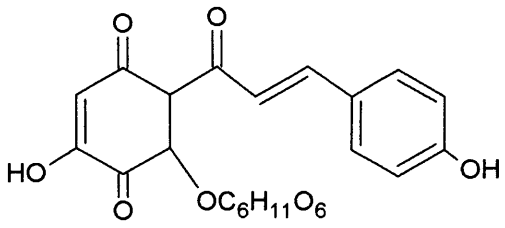

Figure 8.Carthamon

Dyes which include dyestuffs with special chromophoric structures can be classified as **miscellaneous**. An example of this is brazilwood of various origin which, when aluminium mordant is used, gives red to violet colours. Their main compound is *brazilein.* Also, another

important natural dyestuff is logwood, giving black, blue and violet colours, which contains *haematein* as its colouring agent. Finally, turmeric is another well known natural dyestuff for yellow, orange and brown colours and its chromophoric group is *curcumin.*

1.3.d Red natural dyes

Red colour for dyeing textiles is preferred since antiquity and many such examples can be found among historic and archaeological textiles. Many dyestuff providing red dyeings for fibres have been available since 2000B.C (Chenciner 2000, 31). The work presented here is focused on some red dyestuffs for silk, in order to study a category of historic textiles kept and displayed in museums. The red natural dyes chosen to be presented in this section are those identified on original samples used during the experimental procedure *(see also section 7.4.b and 8.1.b).*

Madder

The most famous red dye is madder, which appears to be the most widely used and fast red natural dye. Samples from historic and archaeological textiles from all over the world testify to the extended use of madder. Madder dyeings were in use as early as 450B.C in Mesopotamia and Egypt (Ponting 1980, 135). It is also reported that madder was used by the Greeks in Crete as far back as the 15th century BC and the Later Minoan period. There are also ancient writings mentioning madder as *erythrodanon* (Chenciner 2000, 36). In Europe, it was first cultivated in Italy about 50AD, mostly for wool dyeing, and later in Belgium, Holland, France and Spain (Ponting 1980, 134). The mass production of madder appears by the mid 19th century in central Europe, France and Holland and it was imported regularly to Smyrna and Cyprus. Madder was practically replaced by synthetic alizarin[10] in 1826 (Cannon 1994, 76).

It is the main anthraquinoid dye and has also proved to be as lightfast as the best of the modern dyes (Crews 1987, 69). Madder is also used in dye combinations in order to increase the fastness of other red dyes. The main dyeing component of madder is alizarin and it is contained in many

[10] Alizarin: basic component of anthraquinone dyes, *see also 1.3*

species of the *Rubiaceae* family. The dyestuff is extracted from the roots of the plant that have a reddish orange colour. The plant matures to its maximum alizarin content at the age of 3-5 years. The roots of the plant are cleaned, dried and broken into small pieces ready to be boiled in water and give the dyestuff solution. Because of its wide use it is also called simply "the root" (Ponting 1980, 134). The main ingredients of madder root that gives its colour is alizarin, $C_{14}H_8O_4$, together with purpurin $C_{14}H_8O_5$ and some other colouring matters in smaller quantities (Hofenk-De Graaf 1969, 68).

Madder is the most important mordant natural dye and, as already mentioned, can give different shades depending on the mordant or mordant combinations used. For example, with alum mordant one can obtain pink and red colours, where iron-alum combination usually gives lilac and browns. The obtained colours usually have very good fastness to water and light but without the mordant procedure the dyestuff does not give any colour or gives one of poor fastness (Ponting 1980, 137).

Madder dyeings are preferred for use on cotton and linen as their use on proteinaceous fibres gives less brilliant shades. However, madder red has also been used with alum mordant on silk, giving deep red and orange shades, while madder-cochineal combinations give bright red shades with a bluish cast.

Madder is one of the most lightfast natural dyestuffs and has a very good performance in washing too. Alizarin, the main colouring matter of madder is insoluble in water while purpurin is only soluble in hot water (Hofenk-De Graaf, 1969, 68).

Cochineal

This is an animal dye also of ancient use, particularly in Egypt and the Mediterranean. Its use is also mentioned by the Assyrians and it appears that Ancient Jews also used it (Hofenk-De Graaf 1969, 76). The dyestuff is produced from scale insect of *Coccidae* family and is also an anthraquinoid dye. It was first cultivated in Mexico for dyeing purposes, but very quickly its cultivation was spread to central and south America, the east and west Indies and the Canary

islands (Ponting 1980, 42). The fundamental colouring ingredient in the insect is carminic acid, $C_{22}H_{20}O_{13}$ at a 10-15% concentration (Golikov 1990, 289).

Cochineal produces bright red shades on silk and wool when mordanted with alum and with the addition of cream of tartar[11] (Goodwin 2003, 55) and is a rather expensive and rare dyestuff. It is also a polychromic dye, like madder, as it gives different shades with the use of different mordants and mordant combinations, while depending also on the pH of the dyebath. Cochineal, due to its synthesis, can dye silk not only as a mordant dye but also as a direct and acid dyestuff (Golikov 1990, 189).

Cochineal is similar to the well known dye from antiquity, kermes, but it has a brighter and more stable scarlet red colour and, therefore, soon replaced kermes after the discovery of America where it was available in large quantities (Ponting 1980, 43, Goodwin 2003, 55, Hofenk-De Graaf 1969, 77).

The light fastness of cochineal is relatively good but it has low wash-fastness as carminic acid is easily soluble in water and alcohol (Hofenk-De Graaf 1969, 78).

Brazilwood

Brazilwood belongs to the class of redwoods. More specifically it belongs to the group of the soluble redwoods which are "soft woods", which means that their colouring ingredients can be dissolved in water. In the same family also belong peachwood, sappanwood and other woods coming under the name "brazilwood" (Taylor 1986, 22). Although its name refers to its South American origin, brazilwood was used in Europe long before the discovery of the New World, as it was imported from Asia (Hofenk-De Graaf 1969, 95). In fact, the opposite happened, as the discovery of the brazilwood tree in the new land in large quantities, gave the name to the newly discovered country, known as Brazil today (Hofenk-De Graaf 1969, 95, Ponting 1980, 23, Cannon 1994, 36).

[11] Cream of tartar: Potassium hydrogen tartrate ($KHC_4H_4O_6$), it is a mordant assistant which helps the dye to attach to the fibre in a more permanent state and at the same time allows the use of less mordant (Fereday 2003, 14; Adrosco 1971, 118)

The dyestuff comes from the wood of various species of the *Caesalpina* trees and the main colouring component is brazilein $C_{16}H_{12}O_5$, a flavonoid dye ingredient (Cannon, 1994, 36). The dyestuff's initial form is brazilin and it is transformed to brasilein by oxidation which occurs when cutting large blocks of wood into small pieces (Hofenk-De Graaf, 1969, 97, Cannon, 1994, 36). Other components of the dyestuff are considered to be *haemotoxylin, quercetagetin* and another flavonoid , *ficerin* (Cannon, 1994, 36).

Brazilwood gives a deep bluish red colour to wool and silk when pre-mordanted with alum, with the addition of cream of tartar. It is considered of low light fastness among natural dyestuffs. This is the reason why brazilwood has been combined from early times with madder or cochineal, to improve lightfastness, alter the brightness, and also to reduce the amount of the more expensive fast dye needed for dyeing.

Safflower

Its botanical name is *Carthamus tinctorus* and it is one of the ancient dyes mostly used in India and Egypt. Fabric bandages on Egyptian mummies in the twelfth dynasty were dyed red or yellow with safflower (Cannon 1994, 92), while it was also used for dyeing yellow the robes of the Buddhist priests in India (Ponting 1980, 157). It is also used on dyeing cotton tapes for legal documents, and the expression "red tape" originates from its use (Goodwin, 1982,59). Apart from its name, there is no relation to the well known saffron that safflower replaced in many cases, as it was much cheaper. Safflower is also known as dyer's thistle, or dyer's saffron (Goodwin 1982, 59, Hofenk-De Graaf 1969, 36, Taylor 1989,12).

The flower (petals) of the safflower plant contains two dyes, one yellow and one red. Although the yellow dye produced by safflower is of very low fastness, it was preferred in antiquity to the red, probably because there were other, red dyestuffs of better quality readily available (Ponting 1980, 157).

The colour is extracted from the dried petal of the plant which was easily cultivated around the world. As already mentioned is contains two colouring agents, one yellow in 30%

quantity, $C_{14}H_{16}O_7$, which is usually rinsed off before use. The most important dyestuff exported form the safflower plant is the red *Carthamin* $C_{21}H_{22}O_{11}$ which is only 0.5% of the total dyestuff content. As carthamin is not soluble in water, it stays in the petals while the yellow dyestuff is washed off (Hofenk-De Graaf 1969, 37, Goodwin 1982, 59).

It can be used for dyeing silk and cotton directly from an alkaline water solution which is neutralized afterwards with citric acid, giving a salmon pink shade that none of the other natural red dyestuffs can produce (Hofenk-De Graaf 1969, 37).

Unfortunately its light-fastness, even in the red shade, is very poor in comparison to the natural dyestuffs that can also produce pink and rose shades (Ponting 1980, 157). It has been reported that cotton dyeings have better light stability than silk and, that the lightfastness increases significantly in both fibres, when kept in anoxic environments (Hofenk- De Graaf 1969, 37).

Section summary

In the first chapter three main subjects for this research are presented, the properties and action of light, the silk fibre used to produce textiles of historic value and natural dyes (more specifically reds).

Silk fibre is a naturally occurring protein polymer composed of 16 amino acids linked by peptide groups. Silk was used from antiquity for the production of important textile pieces and its receptiveness to dyeing with natural dyes, giving bright colours, is one of its main advantages for its extended use throughout history.

Natural dyes coming from plants and animals were used for dyeing silk and can be classified according to the method of application and their chemical structure. This study is focused on red natural dyes used on silk fibres in historic textiles. Most of those dyes belong to the class of mordant dyes, where a metal salt is used prior to dyeing in order to assist the fixing of

the dyestuff into the fibres. All, except safflower, belong to the class of anthraquinones which is the most important among natural dyestuffs.

The colour of the dyed textiles is attributed to the selective absorption of visible electromagnetic radiation coming from the sun and reaching the earth's surface. All polymer materials, such as fibres and dyes, absorb light and the energy of the absorbed photons is conveyed to the absorbing polymer molecules. In cases where the amount of energy absorbed by the molecule is greater than the energy of the bonds in the polymer chain, the bonds can be broken and the polymer degraded. Radiation in the ultraviolet, as well as certain wavelengths in the visible spectrum, are capable of breaking molecular bonds and therefore cause photodegradation.

2. Photodegradation and Conservation

This chapter first provides a review of the photodegradation mechanisms of natural fibres and dyes used in historic textiles. It was considered important at this point to study these mechanisms in order to understand the proposed methods of stopping, retarding or preventing them by the action of photodegradation inhibitors as presented in *Chapter 4*.

Following that, a review is given of preventive conservation methods used in modern museums, relevant to light degradation, with the aim of highlighting both their achievements and their limitations. The need for research into another approach on the subject will thereby be established: a preventive/remedial treatment for historic textiles on exhibition.

2.1 Photodegradation

2.1.a Photodegradation of natural fibres in historic textiles

Historic textiles are made of natural fibres, as man-made synthetic fibres were not introduced in the textile technology until the end of 19th century. Natural fibres, either cellulose (e.g. from plants) or protein (e.g. from animals) are naturally occurring polymers. Light degradation of these polymers is a complicated phenomenon as natural polymers have complex molecular structures which in some cases have not been studied thoroughly (Crews -Cox, 1984, Needles, 1981, Randy and Rabek, 1975, Taylor, 1990,Textile Institute, 1975).

The action of light radiation and the photochemical reactions within fibre molecules have been explored previously (*see for example*: Baltova *et al,* 1998, Brill, 1980, Bowen, 1946, Feller, 1994, Giles, 1963, Mills and White, 1987, Nicholson, 1991, Randy and Rabek, 1975, Timar-Balazsy and Eastop, 1998, Tucker et al, 1980,) but it is still under research as it has proved to be affected by many external factors and thus is very complex. The photodegradation process is summarised below:

The fibre molecule contains chromophoric groups. These are chemical structures that have the ability to absorb electromagnetic radiation selectively. The presence of these choromophoric systems in any integral part of the fibres, make it light sensitive as they can absorb visible as well as ultraviolet light. For example carbonyl groups, such as aldeyde and ketone groups are chromophoric groups and their absorbance is close to the visible region (Timar-Balazsy and Eastop 1998, 17). As mentioned above, ultraviolet radiation is capable of breaking molecular bonds, when absorbed by the components of the fibres, causing *photolysis*. If the molecules of the fibres contain weak covalent bonds, visible light may also cause photolysis (Brill, 1980). Table 3 compares the energy of radiation at different wavelengths to the energy of some bonds in the fibre polymers, showing that near-ultraviolet and visible radiation have enough energy to cause photolysis.

*Table 3. Energy of electromagnetic radiation and bond energies present in the polymers of fibres**

* Data taken from Timar-Balazsy- Eastop 1998, 17

Photodegradation starts with photolysis where an atom is separated leaving a very active radical. This radical reacts with atmospheric oxygen. This reaction gives a polymer peroxide

radical which in turn detaches a hydrogen atom from a close molecule forming an hydroperoxide polymer. This step is called *propagation step*. The whole procedure is called *photo-oxidation.*

The photodegradation procedure does not stop here, as there is a series of chemical reactions that can take place without further absorption of electromagnetic radiation, called "dark" reactions and they are totally dependent on temperature.

These reactions involve the peroxide radicals formed before which contain bonds of low detachment energy and can be broken easily by atmospheric heat energy at ambient temperatures. In this way, these radicals can undergo many chemical reactions giving several degradation products. As many of these degradation products of the fibre polymer also contain chromophoric groups, the colour of the fibre will change, resulting in yellowing. Also covalent bonds in the polymer structure undergo rupture (chain scission) and as a result the mechanical properties of the fibres decline until the complete breakdown.

Other elements, such as materials added during finishing or decoration which may absorb electromagnetic radiation, often accelerate photodegradation. Dust particles and enzymes of micro organisms may also act as catalysts of the photochemical reactions. High humidity content in the fibre may accelerate any photochemical activity, during and following the exposure to electromagnetic radiation. The secondary "dark" reactions occasionally act very slowly over time and they are entirely depended on the environmental conditions. These reactions are often called *auto-oxidation*. That is why the colour of the fibres does not necessarily change during exposure times, and a discolouration (yellowing) and mechanical reduction is observed later, for example during storage

2.1.b Photodegradation of silk

Silk fibres are considered to have the lowest resistance of all fibres to degradation from ultraviolet light. Radiation of a wide range of wavelengths (high visible and ultraviolet), can cause

photodegradation of silk fibres (Harris, 1984). It is reported that silk is highly responsive to visible light (after CIE157:2004)12, it usually has a blue wool standard rating 1-3 (*see section 2.3 and 9.2.a*) and can present a noticeable fade after 2-20 years of exposure, even if UV filters are used in the light sources (Cuttle, 2007, 47).

It has also been noted that the light-fastness of a fibre is proportional to its diameter. The larger the diameter of the fibre, the better its resistance to photodegradation, as less radiation penetrates into the interior. It can be assumed that one of the reasons that silk is the most susceptible fibre under light exposure is the fact that it is the finest natural fibre.

The poor light-fastness of silk can largely be explained by the presence of the amino acids phenylalanine, tryptophan and tyrosine in its composition. These amino acids have the tendency to absorb electromagnetic radiation and photo-oxidise easily (Timar-Balzsy and Eastop 1998, 45). The degradation products of these reactions are chromophoric groups, resulting in the discolouration of the fibres. A number of photochemical reactions can occur between these oxidation products and the activated molecules of the amino acids present in the silk fibroin. These can involve the rupture of peptide bonds, hydrolysis with the presence of high moisture in the fibre, or the introduction of cross-links in the polymer chain which result in a less elastic and more brittle product (Crighton 1993, 96).

The sensitivity of silk to light may also be affected by the dyeing process with mordant dyes. The addition of metal salts as mordants shows an increase of fading under light exposure, when alum mordant is used, and loss of physical properties of the silk fibre when iron mordant is present (Yatagai *et al*, 2000, 95). Furthermore the reaction of the dyed silk fibres to electromagnetic radiation is related to the type of dye used each time. On the other hand it is also noticed that the

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12 CIE 157:2004, *Control of Damage to Museum Objects by Optical Radiation*. International Commission on Illumination

same natural dyes used on cotton and silk show different light-fastness and this is attributed to the substrate fibre apart from mordant used (Michalski, 1997, 103).

The pH of the solutions used to treat silk during the manufacturing processes is an important factor in the light stability of silk fibres. Silk is less resistant to light damage between pH6 and pH8. It is also reported that silk shows its maximum light fastness at pH10 (Harris, 1984, Timar-Balazsy and Eastop, 1998).

An example of this is the finishing treatment known as 'weighting' that has been commonly used for the last 300 years throughout the world (Bogle, 1979, Becker *et al* 1987, Miller and Reagan, 1989). The weighting process includes the application of 30-300% solutions of inorganic salts of aluminium, iron, lead, tin, or zinc to the fabric in order to increase the body and weight. This was performed primarily to increase the value of the fabric, as it was sold by weight and not by length. These weighting compounds are highly acidic lowering the pH of the solution below 3. Accordingly, it is obvious that weighted silks are more susceptible to photodegradation. The damage caused by strong acids to silk fibres is severe, and it has been shown that the effects of weighting on silk are much more deleterious under exposure to light than in darkness (Becker *et al*, 1987).

2.1.c Photodegradation of natural dyes on historic textiles

Natural dyes are organic polymers and their photodegradation reactions generally follow the same steps as fibres. Photodegradation in this case is expressed by the fading of the dyes, which is the visual result of all the photochemical reactions acting together. By fading usually one means the loss of colour depth, but in reality the photodegradation reactions on dyes often result in change in the hue of colour, which is not always detectable macroscopically (Giles and McKay, 1963).

As dyes are coloured materials, they absorb certain wavelengths of the visible spectrum, and reflect those that appear as their colour. For example a red dyestuff reflects many of the

wavelengths which represent the red part of the spectrum (630-700nm), whereas it absorbs many wavelengths in the rest of the visible spectrum (*see Table 4)*. The change in colour of a dyed fibre when exposed to light is dependant on certain factors where the more important are the chemical structure of the dyestuff, the physical state of the dye (Giles and McKay, 1963, 554, Crews, 1987, 65) the source of illumination, the time of exposure, and the environmental parameters present.

Table 4. The colours if the visible light spectrum (Bohren and Clothiaux 2006, 214)

With the absorption of electromagnetic radiation, a dye molecule is enhanced to an excited state. To return to its normal state, the dye molecule must dissipate the extra energy as heat or lower-energy radiation (fluorescence), and this characteristic may be used for dye identification[13] *(see section 7.2)*. This is what happens in the most light-fast dyes, whereas the majority of dyes, in their excited state and having excess electronic energy, undergo several photochemical reactions.

Although visible light does not carry enough energy to break molecular bonds within the dye, ultraviolet radiation is often absorbed by the dye molecules and has more than enough energy to break certain bonds in the dye polymer chain. This process is known as photolysis. If, during photolytic action, a chromophoric group of the dye is broken, there is a change in colour.

[13] for example Fluorescence Spectroscopy is used for the identification of natural dyes.

The two separated particles have different colours, usually lighter ones which result in the fading of the dyed textile.

Photo-oxidation is the next step in photodegradation reactions in the case of dyes, as in fibres. The reaction with oxygen transforms parts of the chromophoric systems in the dye molecule into non-chromophoric groups. This results in the production of a lighter colour, and thus a faded dye. The presence of high humidity accelerates the fading effect, as atmospheric oxygen and moisture produce hydrogen peroxide, which is an oxidizing bleaching agent (Bogle 1979, Timar-Bazsy and Eastop 1998).

There is a series of other reactions that can take place while the excited dye molecules try to dissipate their energy. These are dependant on the environmental conditions as well as the substrate which in this case is the fibre. As the fibres themselves can absorb electromagnetic radiation, they can be photodegraded, giving degradation products ready to react with the dye molecules, and vice versa. These reactions are called *phototendering* and *photosensitization* and add a further dimension to the damaging effect of light on textile materials (Brill, 1980, 183, Mills & White, 1987 Van Beek, 1966, 124).

As mentioned above not all dyestuffs have the same lightfastness and this is due to different parameters. In general, most natural dyes are very light sensitive, apart from exceptions (indigo and madder), and it is reported that most naturally dyed textiles displayed in museums under non controlled lighting conditions, have faded completely in less than 50 years (Padfield & Landi, 1966, 181). More specifically in a review table prepared by Michalski (1997) with data taken from different published reports, most natural dyes are more likely to show significant fading in 25 years of exposure in daylight through window glass and in 60 years of exposure even if all UV radiation is excluded.

The structure of the dye molecule is an important factor affecting its behaviour under light exposure. From the different classes of natural dyes, flavonoids seem to be the most sensitive,

anthraquinones are reported to have good lightfastness and indigoids are noted as having the best light fastness properties, the same as some modern synthetic dyes (Giles and McKay, 1963, 556). The light fastness of each particular class is designated by its characteristic framework and some substitute groups attached to it, either increase or decrease the lightfastness properties of the dye (Crews, 1987, 65).

The physical state of each dye is also important especially in hydrophilic fibres such as the natural fibres (Giles and McKay, 1963, 550). It is therefore noticed that dyestuffs in large deposits within the fibres show better resistance to light degradation, than those that are more dispersed.. This seems to happen, as large deposits of dye molecules have less overall surface area exposed to light, than single dye molecules, interspersed within the fibre. On the other hand it is also observed that, even when the dye is entirely in molecular dispersed form, the light-fastness can improve, if the concentration of the dye within the fibre is increased. It is therefore assumed that photodegradation occurs only on the exposed surface of dye particles and the amount of fading is dependent on the size of this surface (Giles and McKay, 1963, 551).

Much research is focused on the relation between light intensity and fading of dyes as well as the time of exposure. Some report that dye fading is not always proportional to the intensity of light and every dyestuff reacts differently, whilst others give more attention to the time of exposure. As a general outcome the important conclusion is that "there is no threshold light intensity below which fading does not occur" (Giles and McKay, 1963, 536, Michalski 1990, 584). This is very important as far as lighting in museums is concerned, as low levels of illumination do not stop photodegradation. At this point is it essential to recall the principle of reciprocity, according to which photodegradation is proportional to the intensity of illumination and time of exposure with the effects being cumulative (Carver 1994, 74) *(see also 1.1.b).*

It is interesting to mention here, that the visible effect of photodegradation on dyed textiles is less noticeable as the time passes and one may think that an already faded object,

because of centuries of exposure, will not fade more. This is not right, as many components of the dye are still present and able to cause noticeable change to the textile if photodegraded (Saunders, 1997, 6).

Another factor to be taken into consideration where historic objects are concerned is the amount of damage that has already occurred in the past in comparison to the rate of future damage. So the sensitivity of an historic textile depends not only on the construction materials, but also on the past exposure, unevenness of damage distribution and the induced visual changes on the object (Muething and Waller, 2005, 237).

Finally, environmental factors are proved to play an important role in the photodegradation of dyed textiles. First of all, the composition of the air around an object usually determines its light stability. Higher concentrations of oxygen increase the fading of some dyes (Giles and McKay, 1963, 566) but the exclusion of oxygen may also cause problems, by accelerating fading (Rowe, 2004, 266). Also, the concentration of air pollutants in the atmosphere such as SO_2 and NO_2 proved to accelerate the fading process of dyed textiles in the museum environment in large cities (Hatchfield, 2002, 40-42, Yoshizumi *et al*, 1991, 133). Finally the role of atmospheric humidity is determinative in light fading, as it is noticed respectively the increase and acceleration of photodegradation of dyed fibres, with the rise of humidity levels (Giles and McKay, 1963, 568).

2.2 Preventive Conservation and its Limitations

It is common knowledge among museum professionals that light threatens their textile collections and conservators are aware that the damage already caused by photodegradation on historic textile objects is not reversible. It is also accepted that as long as textiles are displayed, a rate of change caused by light degradation is inevitable and this is termed *perceptible change*[14] (PC) (Ashley- Smith *et al* ,2002,5).

The role of the conservator in confronting the problem is focused, in the recent years, on risk assessment methods, a way of determination the risk of deterioration for a particular object in a specific environment (Michalski 2004, Waller 1994). Light damage is considered an important risk for textile collections and it is characterized as constant and gradual (Muething and Waller, 2005, 236).

The common practice in museums and historic collections in the recent years is preventive conservation which is mainly focused on controlling the environmental conditions. As presented by Michalski (2004, 65), in order to control the typical agents of deterioration in a museum, among them degradation by light, one should follow some stages of control:

1. *Avoid sources and attractants of the agent.* In case of photodegradation the sources of deterioration are the sun or artificial lighting. On the other hand, attractants of photodegradation include the construction materials of textile objects, as explained before, and also air pollutants, soiling and incorrect levels of humidity and temperature

2. *Block the agent of deterioration.* This is achieved by controlling light sources, illumination levels and time of exposure. Still detection is essential in order to check the effectiveness of the measures taken.

3. *Detect the agent or its effects.* Detection is achieved by analysis, direct testing, monitoring systems and light dosimeters. Even if any museum tries to avoid or block sources of

[14] Formerly termed *"just noticeable change"*, (Ashley-Smith *et al*,2002, 5)

deterioration, practically is not at all times realistic or sometimes stages 1 & 2 fail and detection is always advisable (stage 2-3) (Michalski, 1990(a), 590, Michalski, 2004, 65).

4. *Respond to the agent of deterioration.* This involves the application of methods or strategies in order to respond to the detection of the agent of photodegradation or damage on objects (e.g. re-evaluate, avoid- block strategies, minimize illumination levels, remove dust accumulation on objects etc).

5. *Recover from the effects of the agent on the objects.* In case of textiles suffering photodegradation, recovery involves remedial conservation applications dealing mainly with the improvement of mechanical properties of photodegraded fibres.

From the above mentioned stages the first four are representing preventive conservation while the fifth involves traditional methods of interventive or remedial conservation (Michalski, 1990(a), 589, Michalski, 2004, 65).

As already explained light of any wavelength can be damaging, with UV radiation being more responsible for the photodegradation of organic materials. Visible as well as infrared light carry enough energy to cause degradation to more light sensitive fibres and dyes. The exclusion of light in storage is easily achievable but the same does not apply in display (Thomson, 1986, 22). When an object is removed from storage and placed on display the only parameter of risk or mechanism of change is exposure to light (Raphael 2005, 248).

It is a fact that museums place on display their most important, rare and sometimes fragile objects and by doing so, the collections are placed at a greater risk than if they are kept in the controlled environment of a store room. Also, very commonly museums and exhibitions are housed in buildings that they were not made for this purpose and they do not meet museum standards. Most of the times it seems that the only solution is to isolate objects into display cases, which if properly constructed, the inner environment can be controlled (Raphael 2005, 247). When it

comes to display, modern museums and collections following the stages pointed out before, are using the strategies summarized below.

2.2.a Exclusion of natural light

The first measure to be taken in a museum display for historic textiles is the exclusion of natural light. As the intensity and the wavelength distribution of natural light are very difficult to control in the museum environment, it is preferable to illuminate exhibitions with controlled artificial lighting systems. Still there is a conflict on that, by curators, conservators, designers and visitors as in some cases natural light plays an important role in exhibitions in open houses, palaces and folk art collections (Graham-Bell 1986, 9, Bell 1987).

An example of this is the visibility problems arising when large and light sensitive objects are displayed such as tapestries. In order to enjoy a tapestry in detail and as a whole, lighting imitating daylight is needed, which gives the opportunity to the viewer to examine a detail and at the same time to sit back and admire the whole object. Unfortunately for light sensitive objects such as textiles the use of daylight is prohibitive (Michalski, 1997, 101).

The typical practice in museum buildings is to cancel glazing wherever this is possible. This is achieved by permanently blocking windows or adjusting blinds, heavy curtains and automatic louvres in order to exclude natural light or at least to filter it with UV filters in all glazing (Cassar, 1995, 45,90). An example of partial use of natural light, as important future of the exhibition, is that of the Sainsbury wing at the National Gallery in London. Daylight is entering the display rooms from the roof which is double-glazed with an interlayer of polyvinylbutyral, absorbing all UV radiation (Saunders, 1993, 633).

The uncomfortable feeling of completely closed exhibition space can be overcome by placing perforated metal shutters over glazing, which lowers down the levels of illumination and at the same time permits the view of the exterior (Cassar 1995, 45).

2.2.b Lowering the levels of illumination

Curators and conservators prefer to lower light intensity according to the sensitivity of the objects in display. In the case of historic textiles which fall into the most sensitive category, illumination is suggested to be kept ideally at a maximum of 50 lux . The benchmark of 50lux was set quite early by Thomson (1961) as a compromise between visibility of the objects and their sensitivity to light degradation, although some flexibility was given dependent on circumstances.

Since stable light at all times is a difficult task and totally excludes the use of natural light, some museums allow light variation during the day and the seasons by measuring the total light dose per annum, preferably not to exceed 600 to 650 Klux.h. Even if this limit is met, there is always the conflict on how much photodegradation per annum is acceptable to objects under this light exposure (Saunders, 1997,5). To control daylight to a stable low level of illumination, as the one mentioned, proved to be a very expensive and difficult task (Thomson 1986, 28). Artificial lighting systems, on the other hand, are readily controlled, but it is important to ensure that their wavelength distribution does not cause significant changes on perceived colours (Cassar 1997, 90).

Another consideration on low levels of illumination inside museum showrooms, is the eye adaptation of the visitors which need some considerable time when coming from an external and bright environment. Although 50lux was considered to be a sufficient light level for the perception of colours in a museum room, it mostly applies to young and healthy visitors (under 30 years of age) and only when the illuminated objects have coloured surfaces without low contrast detail (Michalski, 1997,98). Older visitors, especially those with vision problems, may feel discomfort in dark or low illuminated rooms and the adaptation of the eye to the new lighting may take more than one minute. This can be overcome if this adaptation takes place in a lead-up entrance area (Thomson, 1986, 26).

Many museum professionals, other than conservators, argue about these low levels of illumination because of the quality of the light provided in a museum room or case. Conservators

notice that we can see perfectly well details at 10-20lux and at 50lux most of the visitors can see all the important information of an object. The fact is that with more light we can see colours brighter and the perceived photodegradation of objects is the price to pay for this option (Michalski, 1990 (b), 584).

2.2.c Controlling exposure times

The length of time under which a light sensitive object is exposed is of great importance and this is another major concern of preventive conservation. Restrictions can apply on the time of exposure of some extremely fragile objects in large and organized museums, during the winter when light is considered less dangerous (Thomson, 1986, 37). In many cases objects are not displayed to the public and they can only be seen, after special arrangement, by researchers and special personnel. Very often illumination is retained only in the opening hours of an exhibition (Corr, 2000, 23) and very low illumination of 5-10lux is only kept for security reasons for the rest of the time.

The so called rotating display is another method of reducing the time of exposure and it is applicable to large collections of similar objects. In this case the objects are replaced, in regular intervals, by others of the same kind, period and historic importance. This practice cannot of course apply to special and rare objects of a collection (Coote, 1998, 44).

Another suggestion given by Ashley-Smith *et al* (2002) about new lighting policy in the V&A museum in London, is the "highlight days". According to this plan a fragile object can be displayed in higher that 50lux illumination levels (200lux) for one or more days per year, according to its sensitivity and risk assessment. These days are addressed to elderly viewers and those with vision problems who need more light to admire details of the objects.

The idea of illumination only while the object is on view, finds application on more remote or less popular museums. In this case the lights can be turned off where there are no visitors in

the room, or levels of illumination are kept very low. The lighting system may be connected to a time switch either to turn on and off the lights, or simply increase or decrease the intensity (Thomson, 1986, 38). In some organized museums, the lighting system can be controlled by the visitor himself, by activating the system only when he wants to examine an object (Ashley-Smith *et al*, 2002, 7). All the above mentioned systems often have high cost and require regular maintenance and supervision.

Finally, the reduction of exposure times on sensitive objects has given some museums the opportunity to increase the lowest light levels to 80lux in favour of visibility of the objects, but as light degradation is a cumulative phenomenon, one has to accept that some deterioration per annum will be inevitable (Saunders, 1997, 5).

2.2.e Filtering and controlling artificial lighting systems

As the most destructive part of the electromagnetic radiation is considered to be ultraviolet light, the use of filters that absorb UV radiation was considered quite early. These filters are fitted in windows and display cases as interlayers, varnishes or invisible sticker polyester films (Staniforth, 1987, 25).

Also the selection of artificial light sources as well as their positioning in the display helps in the protection of historic textiles from photodegradation. In general low-power tungsten lamps are preferred as they emit low levels of UV radiation (about 75 microwatts per lumen) but still they have to be filtered when the level of illumination is higher that 50lux. Fluorescent lamps are also in use in museums but always wrapped with UV filter acrylic films. "Warm" fluorescent lamps were sometimes preferred because they are less destructive, as they transmit lower levels of radiation, but they produce a redder colour and they increase the temperature as they emit more infrared radiation (Brill, 1980, 26). In case of use tungsten halogen lamps, a heat resistant glass (a dichroic mirror) should be interposed and empowered with UV filter, as these lamps provide high

temperatures while in operation (Cassar, 1997, 93). Still these lamps should never be used inside a display case although they are mistakenly called (cool beam) (Ezrati, 2002, 47) In any case the use of an infrared-rich source such as halogens can have many risks, since the rise of surface temperature on the object's surface can cause expansion and moisture migration. The surface temperature drops again when the lights are turned off in a 24hours cycle and this may be the cause of more severe deterioration (Cuttle, 2007, 41).

Recent advances in lighting technology introduced the use of fiber optics in museum lighting which is rather safe and adequate light source, still expensive though. Fibre optic technology is based on the passing of light through an optical fibre where the biggest part of UV and IR radiation is restricted (Burch and Owen, 1987, 108). As well as providing safe lighting for museum artefacts, fibre optics also give the opportunity to illuminate different objects in the same showcase at different light levels. They use much less energy if properly installed and because of their small size inside the case, they contribute to the good aesthetics of the display promoting the objects. The external maintenance of light source adds security to the environmental stability (avoid frequent opening of the showcase). Still, if fibre optic technology if not used properly the final result may not meet expectations and usually high cost is involved (Bowers, 1997, 106).

At the present LEDs are more and more widely used for lighting in museums, although the CRI (colour rendering index) is not yet appropriate (Ezrati, 2002, 55).

The positioning of the light sources is also important not only from the conservation point of view but also for the better viewing of the objects and the comfort of the visitors. It is therefore preferred to keep light sources and their equipment out of the showcases for the avoidance of high temperatures and easy and safe maintenance. Objects are better to be illuminated from above as this is the way the human eye is used to observe objects illuminated by the sun. Still when large textiles objects, such as hanging tapestries, are displayed in vertical position they may need special consideration. Also any light source must have a relatively wide distance from

the object. Close contact will cause heat and light damage as well as it will exaggerate the texture of a textile or irregularities of an embroidery for example (Thomson, 1986,36).

Although filtering every light source and glazing is a good idea and helps reduce the most harmful radiations, still visible radiation cannot be restricted as filters must be colourless and invisible to visitors. In practice UV filtering materials are not totally effective, as most of the times they do not absorb all UV radiation emitted and they actually absorb small quantities of visible light because they have a pale bluish-grey colour (Thomson, 1986, 34). Varnishes and acrylic films are guaranteed to be effective for only 5-10 years depending on the location, and in sunny countries they do not last as long (Staniforth, 1987, 26,27).

2.2.f Controlling the environmental parameters

As already mentioned photodegradation reactions are also dependent on other environmental factors such as humidity, temperature and air pollution. Controlling these parameters inside museums diminishes the risk of deterioration of textiles in general, but also helps in the retardation of some photochemical reactions too.

An important factor usually taken care of is the rise of temperature during exposure times. All radiation absorbed by the exposed objects is converted to heat and the rise of temperature is dependent to the colour of the object. Darker colours may cause greater rise of the surface temperature (Thomson, 1987, 46). Furthermore all light sources either natural or artificial give out some heat. Preventive conservation is facing this problem by either putting all fragile objects in refrigerated showcases or adjust cooling systems in museum rooms. The acceptable levels of temperature for archival material and textiles are 5 to 10°C, which is more easily obtainable inside display cases or storerooms but not in large museum rooms. Even if this temperature is obtained in museums, one can imagine how uncomfortable this will be for the visitors.

Humidity is the second factor to be considered and its stability is the most important. For historic textiles ideally the acceptable level for relative humidity is 50%RH ±5% but in any case within a range of moderate RH values (30-60%), rapid or large changes should be avoided (Erhardt and Mecklenburg 1994, 37). The desirable levels of humidity are obtained with air-conditioning or the adjustment of humidifying- dehumidifying appliances. This equipment can be fitted in the showcases or is placed in the museum showrooms as free electrical units.

Generally speaking high levels of temperature or relative humidity accelerate the photodegradation of organic materials in addition to causing physical deterioration. Still, at normal room temperature and humidity, the *rate* of change of these two values is more important and must be controlled (Cassar 1994, 74).

The most recent and of course more sophisticated method of controlling both temperature and relative humidity, with additional filtering of air pollutants, is the provision of air-conditioning systems inside display cases. This kind of equipment can be adjusted to the precise needs of the objects in the case and needs regular inspection and maintenance by professionals; it has high cost. Knowing that every category of museum objects needs different environmental conditions, there are restrictions on the placement of objects of different nature in the same showcase. Many considerations also arise when combined objects or groups of objects, belonging to different classes, need to be displayed together (e.g traditional costumes).

2.3 Detection of photodegradation

The detection of photodegradation on a textile collection first of all starts with the assessment of vulnerability of the objects that can help in the prediction of deterioration to be induced under the given parameters. This can be achieved either by the historical analysis of the artifacts or chemical/instrumental analysis of their construction materials (Michalski,1997, 102).

Another method of detection, suggested by CCI[15], is the direct testing on a tiny section of the same object, usually at the back side of a textile or in a hidden area. This small area of the selected textile, having diameter of only 2mm, is exposed to electromagnetic radiation of high energy (200,000lux) and artificial high speed ageing is performed (Michalski, 1997, 102).

The monitoring of light levels inside museum rooms and cases can be done with the use of special equipment such as lux meters and radiometers and the study of their measurements also involve the engagement of specialists. All the above require high cost and specialization and cannot be applied as a routine procedure in every museum or heritage site.

The solution to this problem is the use of sacrificial simulation materials where the effect of induced light degradation can be measured and studied. An example of this type of monitoring is the blue wool standards, where some pieces of wool dyed with fugitive blue dyes are placed next to the object at risk in the display area. Any fading observed in a dyed piece of blue fabric measured against a standard, can indicate the damage caused in the object (see more at section 10.2.a). In this way the term "equivalent light dose" (ELD) is introduced, meaning the "light dose which is capable of producing, in a given material in a uncontrolled environment, the same spectral variation as that measured in the same material exposed under well-defined and controlled environmental conditions"(Bacci et al, 2004, 86).

In recent years, a new product has been introduced for museum testing, known as "light dosimeters", because the blue wool standards were considered not so sensitive and standardized *(Bacci et al, 2004, 96, Romich and Martin, 2003,2).* This system under the commercial name LightCheck® is available in two forms and the one appropriate for more sensitive materials such as textiles (LCU – LightCheck® *Ultra*) are responding to low light exposures below the detection level of the blue wool standard No.1 *(Bacci et al, 2005, 569).*

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[4]Canadian Conservation Institute

2.4 The role of remedial conservation

Practical procedures have been used over the years to deal with already photodegraded historic textiles with variable success. Practice and research has shown that the fading effect of dyes caused by light degradation is non reversible and there is nothing one can do to return a faded textile to its original hue or depth of colour. The main effort in textile conservation was given from the early years on enhancing the mechanical properties of photo-degraded fibres, their humidification, stabilization and sometimes the bleaching of white textiles which had yellowed due to photodegradation. The above mentioned methods involve the use of additives, chemical treatments and application methods that are active, time consuming and most of the times non reversible or hazardous. The detailed presentation of conservation methods are beyond the scope of this research, but some of the methods are presented in brevity, in order to illustrate how devastating light damage is to fibres and how complex remedial conservation can be.

Humidification techniques are widely used in textile conservation and involve all these methods applied in order to increase the moisture content of the fibres which was either lost because of degradation (for example dryness due to photodegradation), or in order to ease creases and other distortions (Hughes and Wolf 1993). In such case water plays the role of plasticizer improving the flexibility of the fibres (Cooke 1988).

Humidification techniques allow the introduction of water into the fibres in the form of individual molecules in order to minimize the risk of mechanical damage by the forcible entrance of large group of water molecules in liquid state. This procedure is irreversible and interventive and demands special equipment (e.g. ultrasonic humidifier) and long time of application.

Since textiles are hygroscopic materials, humidification techniques are not without risks. Water sensitive materials can be affected by the presence of water; binding media in paints, printing inks, dyes, metals, water soluble sequins are some examples given by Timar-Balazsy and Eastop (1998).

Consolidation is a method used in textile conservation in order to endorse deteriorated fibres and improve their physical strength, very often lost by photodegradation. This is achieved by the introduction of consolidants into the fibres. Consolidants are substances in liquid phase which are subsequently solidified. Many such materials have been tested and used over the years with questionable results (*see for example:* Allington 1995, Berry *et al* 1977,Delacorte *et al* 1971, Hersh *et al* 1982, Hutchins *et al* 1981, Finch 1963, Landi 1992, Lodewijks 1965) and it is not rare to report that several consolidants caused more degradation of silk fibres than improvement of mechanical properties upon ageing (Masschelein-Kleiner and Bergiers 1984).

Consolidation of fibres is considered only in the case of highly degraded fibres, and especially silk, caused by several degradation factors and very often by severe photodegradation, as the methods and materials used are practically non reversible. The consolidated fibres, even if the application is considered successful, are still in very fragile state and need special conditions for storage and display as the ones mentioned above. An example of this is the use of Parylene C tested on very fragile textiles with promising results (Grattan and Bilz 1991, Hansen and Ginell 1989, Halvorson and Kerr 1992) but still reported to be very sensitive to ultraviolet radiation, showing yellowing of the treated fibres upon exposure to light in a short period of time.

Stabilization and support of photodegraded silk fibres with new fabrics is a common practice in textile conservation in order to exhibit an object. The techniques usually applied involve more often the use of adhesives, in the case of fibres made brittle by photodegradation, rather than stitching techniques. When using adhesives, a support lightweight fabric is coated with adhesive which is left to dry to form a thin film. The adhesive coated support is applied to the deteriorated area and the joining of the two layers is achieved by heat sealing or solvent evaporation techniques (*see for example*: Gill and Boersma 1997, Landi, 1973, Reeves 1977).

Many adhesives have been tested and used over the years in textile conservation, subject to conservation criteria such as flexibility, resistance to ageing, not yellowing or giving out

damaging degradation products, retention of solubility in terms of retreatability of the adhesive without damaging the textile, and finally not damaging the fibres and dyes in any way (*see for example*: Ekhorth-Edebo and Peteus 1993, Robson 1988, Senvaitiene *et al* 1981). However, many considerations and debates have taken place on the use of adhesives in degraded historic textiles, because many of the above requirements are not satisfied (*see for example*: Finch 1982, Jedrzejewska 1981, Keyserlingk 1990).

Finally, pressure mounting techniques are preferred in recent years as limited interventive support solutions for the display of flat deteriorated textiles and fragments (*see for example*: Bacchus and Lord 2000, Giuntini and Bede 1994, Kajitani and Phipps 1986).

The use of oxidizing and reducing agents in textile conservation, treatments also known as bleaching, were for many years common practice in order to obliterate the yellowing effect of photodegraded fibres (*see for example*: Block 1988, Burges and Hanlan 1980, Burges 1982, Leene 1972, Ringaard 1995) . Bleaching is a destructive process and it should not be used on any dyed textile. Although several attempts have been made to control the treatments to cause minimum deterioration, it is accepted worldwide that damage to fibres cannot be avoided. During these processes the main aim is to change the chromophoric groups of yellowed textile materials (fibre polymers) so that their length decreases and as a result they are giving a lighter colour (Timar-Balazsy 1998, 225). The carbonyl chromophoric groups of the fibre molecule are transformed into non chromophoric carboxyl groups or hydroxyl groups and the yellowing process is reversed. Bleaching is mainly used for cellulosic fibres as fragile protein fibres such as silk would not survive the procedure.

Section summary

Photodegradation of natural fibres and especially silk and dyes includes a series of chemical reactions induced by the absorption of electromagnetic radiation by the polymers (fibres and dyes). The general steps of photodegradation are photolysis (chain breaking), photo-oxidation and auto-oxidation (dark reactions). Silk is considered the most susceptible fibre to light due to its fine diameter and its synthesis.

Photodegradation reactions are dependent and abetted by the environmental conditions such as humidity, temperature and air pollutants as well as impurities in the textile surface and finishing treatments. The results of photodegradation on historic textile materials and dyes are observed by yellowing and discolouration of the fibres, loss of mechanical strength and fading of the dyes.

Conservation techniques cannot reverse the photodegradation effects on historic textile materials. Remedial conservation can partially help by improving the mechanical strength of fibres, but the results and methods are questionable. Preventive conservation includes methods of protecting historic textiles by retarding the photodegradation effects, facing a number of limitations. Exclusion of natural light in exhibitions, lowering the levels of illumination and exposure times, controlling artificial lighting and environmental parameters are the methods used and demand constant supervision, measurements, special equipment and usually high cost.

3. Introduction to the Present Research

Until now, no applied method of protection from photodegradation has been routinely used in conservation practice for historic textile materials. Only preventive conservation measures are often practised on textile collections in organized museums, involving the control of display and the storage environment, as presented briefly in *Chapter 2*. Fragile historic textile objects and especially those made of silk, the most sensitive natural fibre under light exposure, would benefit from a protective treatment against photodegradation, under the conservation requirements and restrictions.

Photodegradation inhibitors are materials developed in the modern polymer industry in order to prevent or retard photodeterioration of polymers (*see Chapter 4*). Some of them have been tested and successfully used in the modern textile industry for the production of synthetic textiles and dyes for use in outdoor applications. The effect of inhibitors when added to fibres, has been tested several times in the past as well as on fibres dyed with synthetic dyes (*see section 4.1.a)*. There are also attempts to add them to dye solutions during dye baths and they have also been tested on naturally dyed fabrics *(see section 4.6)*. Photodegradation inhibitors have also been tested for conservation purposes such as additives on protective coatings, varnishes and adhesives *(see section 4.2)*. The question that arises is: can these materials be used on historic textiles?

The basic idea of this research is to explore the possibility of using photodegradation inhibitors as a conservation treatment for historic textiles subject to photodegradation. The reality of the situation is complex though, as hardly any historic textile is dyed with one dyestuff alone, but with dye combinations in order to achieve the desirable colour. Not all textile fibres have the same sensitivity to light degradation and in many cases different types of fibres are mixed in the same object (costumes), in the same piece of textile (embroideries) and even in the same textile weave. The dyestuff mixtures in association with the type of substrate (fibres) may affect negatively or positively the lightfastness of a textile. Moreover, environmental parameters such as temperature, humidity and air pollutants, also play a fundamental role in the reaction of historic textile objects to electromagnetic radiation, as already explained in *Chapter 2.* Finally, historic textiles are already degraded before reaching a museum collection, and their degradation products as well as the chemical changes in their structure are unquestionably interfering in the photodegradation process. All the above mentioned parameters constitute the complexity of photodegradation on historic textiles and affect the approach needed.

Despite their good performance in the modern textile industry, the possible use of these additives as a conservation treatment gives rise to many considerations. The materials should follow some basic conservation rules and this means briefly that they should not affect in any way the colour, texture or mechanical properties of the treated textile. The application methods of selected inhibitors are of great importance, as with historic textiles the treatments must be delicate and discriminating, giving special attention to solvents used as well as the handling of fragile objects. They should not be toxic and must be easily applied in a conservation laboratory. Since photodegradation inhibitors may operate as sacrificial materials, in order to protect the substrate from harmful radiation, it is important to evaluate their own photodegradation and its effect on fibres and dyes. They should preferably be easily removable at any time, meaning that they can be removed from the object without damaging it or altering its properties, since this is an

important aspect of conservation ethics *(see section 5.3).* Finally, it is reported that some photodegradation inhibitors present a synergetic effect when mixed together, and this is a point that needs investigation, in the case of museum textiles.

Summarizing the above, the purpose of this research is: a) to evaluate the suitability of photodegradation inhibitors for use in textile conservation under the posed requirements; b)to investigate the effect of inhibitors on the properties of fibres and dyes; c) to evaluate the ability of selected inhibitors to increase the light-fastness of historic silks dyed with particular natural dyes and dye combinations; d) to investigate if there is a synergetic effect of some inhibitors if mixed together, resulting in better protection of historic textiles; e) to appraise the effectiveness and impression caused by the use of these materials, according to the present conservation practice and ethics.

4. Photodegradation Inhibitors

4.1 Photodegradation inhibitors in the polymer industry

By outlining the mechanisms of photodegradation in *Chapter 2*, it was shown that in order to achieve any form of photostabilization of historic textiles and dyes, the retardation or elimination of some photochemical reactions is needed. A number of approaches to polymers photostabilization have been reported over the years (*see for example*: Carisson and Whiles, 1975, Chirinos Padron, 1989, Chirinos Padron, 1990, Coleman and Peacock, 1958, Decker and Zahouily, 2002, Gantz & Sumner, 1957 , Ghiggino, 1996, Khoromskaya *et al,* 1992, Kikkawa 1995, Kuramoto, 1990, Lappin, 1971, Randy & Rabek, 1975, Rene de la Rie, 1988, Rytz *et al,* 1994, Rytz *et al,* 1997, Shlyapintokh, 1981, Shlyapintokh, 1983, Wiles and Carlsson, 1980), which use materials called photodegradation inhibitors, photostabilizers, UV stabilizers or light stabilizers. Their action is focused on the termination or elimination of the effects of UV radiation on polymers, which is the most destructive part of solar radiation.

As reported in the literature, several types of photodegradation inhibitors are used in the modern polymer industry. In some cases their use is a routine process in the production of materials for everyday use. An example is the use of inhibitors in the production of sun protecting fabrics for canopies, umbrellas and protective clothing (Hilfiner *et al* 1996) as well as sunscreen lotions (Damiani *et al* 2006).

The first approaches to the use of inhibitors for the photostabilization of polymers date to the early 1960s. Their development and extended use is evident in the research literature as well as in the commercial production of these materials by several multinational chemical companies.

4.1.a Photodegradation inhibitors – testing on dyes

Some research has been carried out on using photo-inhibitors to prevent the fading of primarily synthetic dyes and colourants. Tsatsaroni, Eleftheriadis *et al* (1997, 1998, 2004) have written several papers reporting their work on the use of inhibitors for the improvement of disperse dyes when dyeing polyester.

Another paper by Mason *et al* (1991) focuses on the production of a new specific disperse dyestuff, namely the C.I Yellow 86, in which photo-stabilizing agents have been incorporated into the dyestuff's backbone. Oda and Kitao (1991) successfully tested inhibitors, for the photo-protection of indicator dyes in pressure or heat sensitive recording systems (*see also*: Jinjin 1991, Kehayoglou *et al* 1997, Kitao 1991, Kuramoto, 1990, Moura *et al*, 1997, Oda 2001, Oda 2005). The above mentioned testing was designed for the construction of extremely lightfast synthetic dyes destined for the production of new coloured polymeric materials.

4.1.b Photodegradation inhibitors – testing on plastics and other organic polymers

Substantial research has also focused on the use of photo-stabilizing materials on acrylic coatings or varnishes in order to apply them on several surfaces, preferably transparent, and create protective screeners for other light sensitive materials. An excellent example is given by De la Rie and McGlinchey (1990b) in their paper about light stabilization of dammar and mastic picture varnish by the addition of photodegradation inhibitors. After artificial aging tests, they concluded that the stabilized dammar varnish will retain its transparency and solubility even after 136 years of exposure at 1,000lux, provided that UV radiation is excluded.

Another interesting paper on the subject is that of Vigo and Wyatt (1981) in which they present the addition of some ultraviolet inhibitors on cellulose acetate films. These films were

tested for the protection of blue wool standard fabric[16] (AATCC L-4 standard) from fading. It is important to notice here that this standard fabric represents medium light stability of textile materials and is more relevant to the light stability of most natural historic dyestuffs *(see also section 8.3.b)*.

A more recent application of photodegradation inhibitors is presented by Edser (2002) who experimented with the addition of inhibitors to agricultural plastic films used to protect plants in greenhouses and open ground. In this case, UV stabilizing additives on the plastic films helped control the light available for plant photosynthesis (*see also*: Bauer *et al*, 1990, Bourdeau, 1988, Bourdeau, 1990, Decher *et al,* 1995, Decker and Zahouily, 1998).

Photodegradation inhibitors also find application in the modern polymer industry in the production of plastics used for several purposes. Allen *et al* (1981) for example, have experimented with polypropylene after the addition of inhibitors, Gijsman *et al* (1993) used some types of inhibitors for the improvement of mechanical properties on polyethylene films, while Kikkawa (1995) introduces the use of photodegradation inhibitors on recycled plastics for automobiles which are subject to higher temperature processing and increased use in exterior applications (*see also*: Allen *et al* 1989, Edser 2002, Efimov *et al* 1983, Fechine *et al* 2002, Gugumus 2002).

There have also been attempts to photostabilize natural organic materials such as wood. Williams (1983) used an inhibitor in a clear exterior coating on western redcedar unfinished wood, to improve the photochemical stability and the colour retention of the wood surface when exposed to electromagnetic radiation, and many wood coatings now contain photo-inhibitors (*see also*: Chang and Chou 2000, George *et al* 2005, Hayoz *et al* 2003).

Finally photodegration inhibitors were tested on natural textile fibres such as cotton, silk and especially wool (*see for example*: Becker *et al* 1989, Carr *et al* 1985, Cegarra *et al* 1972, Czajkowski *et al* 2006, Cristea and Vilarem 2006, Evans and Waters 1981, Head and Lund 1969, Hilfiker *et al* 1996, Leaver 1982,

[16] Blue wool standards are pieces of wool dyed with specific dyestuffs of known light fastness (*see also 10.2.a*)

Reinert and Thommen 1991, Riedel and Hocker 1996, Rose *et al* 1961, Walden and Moore 1961, Waters and Evans 1983, Waters *et al* 1980).

4.2 Photodegradation inhibitors in conservation

The extensive research on the industrial application of photodegradation inhibitors to natural fibres actuated the primary idea of this study, which is to examine the possibility of using inhibitors for the photo-protection of historic textiles, as all of these studies have concentrated on the production of new, extremely light-fast fabrics, and have not addressed the issue of historic textiles.

The application of photodegradation inhibitors in conservation science is still at an early stage. There are some examples of their testing in conservation, but not on historic textiles. Varnishes, and especially picture varnishes used in conservation, cover the wider range of research on the subject. Several types of inhibitor have been tested on varnishes in order to improve their light stability and increase their protective abilities for the objects of art they are applied on. Bourdeau (1990) used photostabilizing materials for the improvement of longevity of dammar resin. This resin is preferred by paintings conservators because of its "ability to saturate leached oil-paint films and provide an attractive varnish gloss" (Bourdeau 1990, 165). De la Rie and McGlinchey (1990b) also agree that the use of photodegradation inhibitors on picture varnishes made by dammar resins, is a method of preventing yellowing, hazing, cracking and changes in solubility (*see also:* De la Rie and McGlinchey 1990a, De la Rie and McGlinchey 1989, Potje 1984, Lafontaine 1981).

Other attempts on the use of inhibitors for conservation purposes are presented by Douglas (1991) who discusses the use of additives on adhesives and sealants in order to increase their resistance to photo-induced degradation. Nelson and Wicks (1983) are finally presenting the possibility of use of UV stabilizing materials on polymers used in conservation.

4.3 Photostabilization mechanisms

The photo-stabilization of organic polymers with the use of photodegradation inhibitors, can be achieved in several ways, as presented below:

- Screening incident radiation by the inhibitor: during this process the photo-stabilizing mechanism relies on the prevention of the penetration of radiation into the inner parts of the polymer. This way, the degradation process is limited to the external surface of the material.
- Absorption of radiation by the inhibitor: during this process the inhibitor absorbs ultraviolet radiation as well as visible light of longer wavelengths. As a result, harmful radiation never reaches the surface of the protected polymer.
- Elimination of photo-oxidation reactions: in this case, the inhibitors react with radicals responsible for the propagation steps of the photo-degradation process of the polymer.
- Quenching mechanism: during this process the inhibitor, also called a quencher, disables the excited states of the irradiated polymer itself.

According to the available literature, photodegradation inhibitors can be classified into three major groups, according to their mechanism of polymer photostabilization. These are the ultraviolet absorbers, the antioxidants and the excited state quenchers.

4.3.a Ultraviolet Absorbers

Ultraviolet absorbers, as their name indicates, are materials that absorb highly in the ultraviolet region of the spectrum. Their effectiveness is based on blocking the ultraviolet light before it reaches the polymer; hence they are also called screening agents. Since the UV absorbers must be colourless, they should not absorb in the visible region, but must have a high absorption at 290 to 400nm - the ultraviolet section of the spectrum (Lappin 1971).

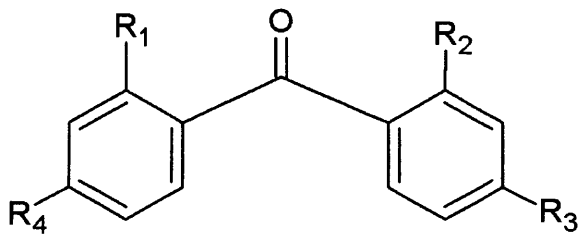
There are many organic materials that may absorb in the ultraviolet region, but not all of them can act as photodegradation inhibitors. An effective inhibitor, when irradiated and photo-excited, must have the ability to return to its ground state by disposing of the excitation energy as heat. If the excited molecules of the inhibitor are capable of returning to the ground state very quickly, with the loss of heat energy, no photochemical reactions can occur. Since these compounds absorb ultraviolet light so strongly, they must be stable to long term and repeated exposure to this light.

Although there is no commercial absorber that has all of the above ideal characteristics, there are some commercial materials that perform quite satisfactorily in increasing the light-fastness of polymers. The most important of them are reviewed next.

Derivatives of 2-hydroxybenzophenone

The most extensively studied absorbers are the derivatives of 2-hydroxybenzophenone (*see for example*: Cegarra and Ribe 1972, Coleman and Peacock 1958, Becker *et al* 1989, Gantz and Sumner 1957, Head and Lund 1969, Jinjin and Griffiths 1991, Mason *et al*, 1991, Reinert and Thommen 1991, Tsatsaroni *et al* 1997, Williams 1983). Their basic structure is given in Table 5, where R_1, R_2, R_3 and R_4 vary according to different commercial products:

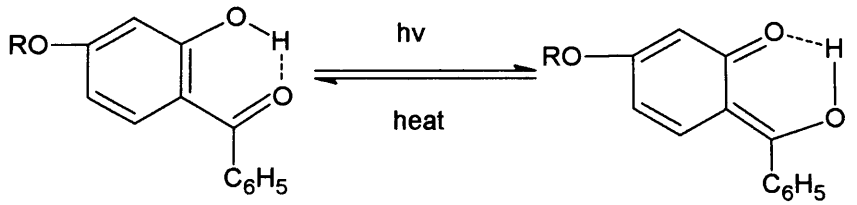
*Table 5. Basic structure of benzophenone UV absorbers and some commercial products**



Commercial product	R_1	R_2	R_3	R_4
1	OH	OH	OMe	OMe
2	OH	OH	OH	OH
3	OH	H	H	OMe
4	OH	H	H	$C_8H_{16}OH$
5	OH	H	H	$C_{12}H_{24}OH$

* Data taken from Mason et al (1991), 115.

This class appears to have strong absorption in the solar ultraviolet range and its effectiveness can be explained by the rapid phototautomerism of its excited states. The (Ia) state is rapidly transformed to (Ib) after the absorption of radiation and then this returns to (Ia) state losing energy as heat with almost 100% efficiency (Lappin 1971, 131) *(see Figure 9).*



Ia Ib

Figure 9.Tautomerism of the excited states of the hydroxybenzophenones

The photochemistry of 2-hydroxybenzophenones has been more extensively studied than that of other classes of ultraviolet absorbers and several studies on fibre and dye testing have been published over the years (*see for example*: Becker *et al* 1989, Cegarra *et al* 1972, Head and Lund 1969, Jinjin and Griffiths 1991, Mason *et al* 1991, Rose *et al* 1961,Tsatsaroni and Eleftheriadis 2004).

In the study by Becker *et al* (1989), a commercial UV-light absorbing benzophenone showed a good performance on protecting silk fabric from discolouration after artificial ageing by light and heat.

A primary study on the use of benzophenones on wool fibres is that of Cegarra *et al* (1972) where it was concluded that the inhibitor tested had decreased the yellowing of wool fibres. It was also noticed that the higher the concentration of the inhibitor the lower was the yellowing of the fibres. As the study was intended for the production of new more stable wool fabrics, the wash fastness of the additive was investigated and it was considered poor. This means that the inhibitor was water soluble after application and it was noticed that this feature

could be improved by previously mordanting[17] wool fibre with aluminium salts. Although the poor wash fastness revealed by these tests may be a disadvantage when producing new fabric, it can be a valuable feature when used on historic textile materials, due to the ease of reversibility and re-applicability of the additives *(see more about the subject in section 5.2 and 5.3).*

The testing of inhibitors belonging to the group of benzophenones on cellulose fibres is presented by an early study of Head and Lund (1969), who tested some commercial UV absorbers, well-established for their use in synthetic-polymer fibres, on cotton. From all the compounds tested, only 2-hydroxy-benzophenone derivatives gave considerable protection against light. Unfortunately, it was also reported that the effect of protection was not persistent as the absorbers seemed to be insufficiently stable to light, especially in hot climates.

Reinert and Thommen (1991) tested benzophenones on polyester and polyamide fibres and indicated the increase of photostability of these fibres when used in intense light at high ambient temperatures (carpets, textiles for automotive interiors, sails, etc). They also noticed that the addition of inhibitors to polyester when dyed in pale and medium shades provided more noticeable results since polyester fibres in deep shades exhibit better light stability anyway (Reinert and Thommen 1991).

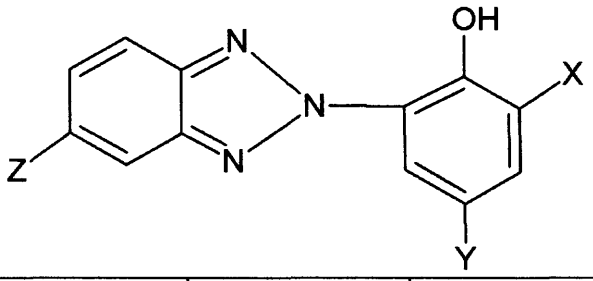
Derivatives of hydroxy-phenylbenzotriazoles

The second most widely applied member of the absorbers group is hydroxy-phenylbenzotriazoles extensively tested for use on polymeric materials (*see for example:* Becker *et al* 1989, Bourdeau 1988, Carr *et al* 1985, Evans and Watres 1981, Head and Lund 1969, Leaver 1982, Mason *et al* 1991, Reinert and Thommen 1991, Riedel and Hocker 1996, Tsatsaroni *et al* 1997, Waters *et al* 1980, Waters and Evans 1981). Like hydroxybenzophenones they may form internal hydrogen bonds and they stabilize polymers by the tautomerism of the excited states (Lappin 1971 , Randy and Rabek 1975). This category of absorbers includes some Tinuvin commercial products produced by CIBA Geigy

[17] See more about mordant dyes in section 1.3.c and mordanting in section 8.2.a

and they are the most widely used photostabilizing agents in the modern polymer industry. Their fundamental form is given in Table 6 where X, Y and Z vary according to commercial data:

*Table 6. Basic structure of Benzotriazole UV absorbers and some commercial products of the Tinuvin line**



Commercial product	Tinuvin	X	Y	Z
1	P	H	Me	H
2	PS	H	t-Bu	H
3	320	t-Bu	t-Bu	H
4	326	t-Bu	Me	Cl
5	327	t-Bu	t-Bu	Cl
6	328	t-Amyl	t-Amyl	H

* Data taken from Mason et al (1991), 115.

The level of protection achieved by the application of these stabilizers is also dependent on their concentration and on the nature of the fibre (Evans & Waters 1981). This means that every fibre type, according to its synthesis and light fastness would react differently to the application of inhibitors.

It is also important to notice that o-hydroxy phenylbenzotriazoles are colourless and very effective photo-inhibitors in various commercial polymers (Randy and Rabek 1975). This characteristic can prove useful for their use on museum textiles, as during the conservation process it is important not to interfere with the appearance of the object *(see also section 5.1).* Hydroxy phenylbenzotriazoles also have higher absorbance in the ultraviolet than 2-hydroxybenzophenones and a higher long-wavelength cut off (Lappin 1971, Mason *et al* 1991).

Several studies on the use of derivatives of benzotriazoles as photodegradation inhibitors for fibres and dyes are reported (*see for example*: Becker *et al* 1989, Carr *et al* 1985, Evans and Waters 1981, Head and Lund 1969, Kehayoglou *et al* 1996, Leaver 1982, Riedel and Hocker 1996, Tsatsaroni *et al* 1998, Tsatsaroni and Eleftheriadis 2004, Waters *et al* 1980, Waters and Evans 1983). The most extensively tested of

natural fibres is wool where benzotriazole absorbers have shown some positive effects. Waters *et al* (1980) for example experimented with 2-(2'-hydroxy-5'-methyl-phenyl)benzotriazole sulfonate on woollen fabric, applied to the textile following a procedure similar to dyeing (aqueous solution and high temperatures). The authors proposed the use of absorbers of this type to woollen fabrics destined for drapes and curtains. They proved that the yellowing of the fibres was retarded. At the same time it was pointed out that the performance of the additive when the textile was exposed to sunlight was much inferior to that in artificial ageing tests. This observation poses several considerations regarding the use of artificial ageing tests for conservation purposes. It is often observed that the complexity of historic textiles, in conjunction with the uncontrollable electromagnetic radiation coming from the sun, cannot be imitated by any artificial ageing test.

Furthermore, Carr *et al* (1985) conclude, after testing sulfonated UV absorbers of the benzotriazole type on wool, that the additives present a sufficient screening power to protect wool against photo-yellowing in sunlight, but their photoprotection ability is reduced with prolonged exposure. In a later study by Riedel and Hocker (1996), however, the tested polymeric UV absorbers derived from hydroxyl-phenyl-benzotriazole proved to be the most effective in protecting wool from photo-yellowing as well as in improving the abrasion resistance and tensile strength of the fibres.

Phenyl esters

The last commercial category of ultraviolet absorbers is the phenyl esters. The most important members of this group can be considered to be *resorcinol monobenzoate* (A) and *phenyl salicylate* (B) *(see figure 10, 11).*

An Evaluation of Photodegradation Inhibitors in the Conservation of Naturally Dyed Historic Silks

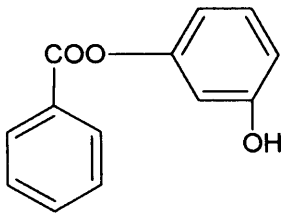


Figure 10.Basic structure of resorcinol monobenzoate

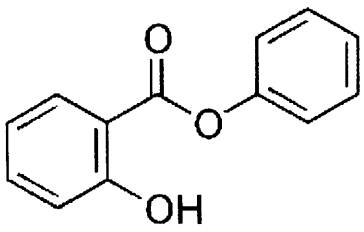
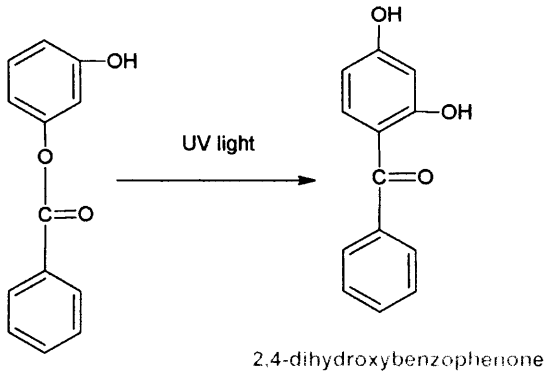


Figure 11. Basic structure of phenyl salicylate

A surprising characteristic of these compounds is that they do not absorb highly in the ultraviolet! However, after prolonged exposure to electromagnetic radiation, their absorption increases significantly in the 290-400nm region and Lappin (1971) states that their UV absorption spectra resemble that of 2-hydroxybenzophenones. It is concluded therefore that their photostabilization mechanism is based on the fact that ultraviolet light catalyses a rearrangement to 2-hydroxybenzophenones and that the products of such rearrangement are the actual inhibitors. An example given by Lappin (1971) is that resorcinol monobenzoate is converted, after exposure to light, to 2,4-dihydroxybenzophenone, which is a very effective UV absorber as mentioned above *(see Figure 12).*



resorcinol monobenzoate

Figure 12. The conversion of an phenyl ester to a UV absorber

It is also noticed, however, that during this procedure other products are produced that may act as catalysts to photodegradation. Only 50 to 70% of the formed products can be considered to be effective inhibitors (Lappin 1971). In this case, it is obvious that these materials are unsuitable for use on museum textiles. Nevertheless, the salicylates were the first stabilizers to be used in practice and they were used extensively on polymer materials, because of their availability and low cost (Randy and Rabek 1975).

No evidence for the testing of these UV absorbers on textile fibres or dyes has been noted in the literature, probably because of the superiority of the benzophenone absorbers. It is also mentioned by Randy and Rabeck (1975) in their study of the photostabilization of polymers that most of the phenyl ester absorbers turn yellow after prolonged exposure to light and *"...this limits their use as ultraviolet absorbers for colourless and transparent plastics"*. It is therefore apparent that their use on museum textiles is inappropriate.

Some other types of UV absorbers were presented in the literature that do not find yet much application, but some of them were tested on fibres and dyes in order to improve their light stability. Lappin (1971) presents *substituted cinnamic acid derivatives* which are not effective photodegradation inhibitors as their absorption in the UV region is restricted between 310 and 320nm. On the other hand this type of absorber shows stability in the ultraviolet radiation and their effectiveness is dependent on the nature of the polymer applied on. The most important characteristic of this type of absorber is its complete transparency.

Oxalanilides is another type mentioned by Mason *et al* (1991) that have maximum absorption at 300nm and show signs of extremely high stability under ultraviolet radiation due to their short lived excited states. After the absorption of radiation the energy is rapidly dissipated through intramolecular proton transfer. This type of absorber can not act as free radical scavengers because they are very stable to free radicals.

A more recently presented type of UV absorber with relatively positive results is some derivatives of triazines. The *2-(2-hydroxyphenyl)-1,3,5-triazines* are mentioned by Rytz *et al*

(1994) as absorbers of high performance and thermal stability developed for use in coatings, plastics , automotive coatings and colour photographic paper. Later, Rytz *et al* (1997) explain theoretically the superiority of *2-(2-hydroxyphenyl)-1,3,5-triazines* against 2-*hydroxyphenylbenzotriazoles* when used for the photostabiliation of polymers, testing two commercial products (Tinuvin 1577 and Tinuvin 360). The two products showed similar protective ability but the first was far more stable to longer exposure periods.

A recent study by Czajkowski *et al* (2006) presents the use of derivatives of *monochlorotriazine* for the photoprotection of cellulose fabrics. These types of inhibitors are not commercial materials but synthesized in the laboratory for research purposes, showing an increase in the UV- protection factor of cotton fabrics.

4.3.b Antioxidants

The second important class of photodegradation inhibitors, the antioxidants, act in several different ways, according to their composition. As the name indicates, their photostabilization mechanisms are based on the elimination of photo-oxidation reactions. Their mechanisms of photostabilization involve direct chemical reaction with radicals responsible for the propagation steps and/or the hydroperoxide groups. The fact that they have proved successful for different types of polymers, such as polyamides, polyesters, PVC, cellulosic polymers, rubbers, polyurethanes and synthetic fibres, shows that they do not operate by interaction with the polymer itself but with the agents of photo-oxidation (Nicholson 1991). There are two ways that the antioxidant mechanisms can be explained:

Reaction with peroxide radicals

The first general mechanism, by which the antioxidants perform their photo-inhibition function, is as reactants with peroxide radicals. They compete with the polymer, in reacting with peroxide radicals, and in doing so they prevent the photo-oxidation of the polymer caused by reaction with

peroxide radicals. Compounds that act in this way include substituted phenols, secondary aromatic amines, quinones and several compounds containing unpaired electrons. They are usually known as kinetic chain breaking (CB) antioxidants. Using an example given by Chirinos Padron (1990), phenols usually react with peroxide radicals to form a hydroperoxide and a phenoxyl radical and the subsequent reactions involving this radical are responsible for the antioxidant ability of phenols.

Decomposition of hydroperoxides

Another way by which antioxidants act to stabilize polymers is through the decomposition of hydro peroxides. The hydroperoxide groups in the photo-excited polymer undergo fragmentation during photodegradation reactions. Using antioxidants, this action is prevented as the hydroperoxides are made to decompose in a different way. This type of additive includes organic phosphates, some metal chelates and several sulphur compounds. They are referred in the literature with the name preventive peroxide decomposers (PD) (*see for example*: Allen 1981, Becker *et al*, 1989, Chirinos Padron 1989, Nicholson 1991, Rytz *et al* 1994).

PD antioxidants include three types of compounds which work with different mechanisms:

- The first type, stoichiometric peroxide decomposers (PD-S), function by reacting stoichiometrically with hydroperoxides by reducing them to inert products and includes organic phosphates and some nickel chelates.
- The second type, catalytic peroxide decomposers (PD-C), decomposes hydroperoxides with a catalytic mechanism and includes several sulphur compounds, cyclic phosphates and arylamidophosphites.
- The third type functions by interaction with hydroperoxides in similar ways as the two previous types, but do not involve stoichiometric reduction of hydroperoxides to alcohols.

Hindered Amines

The third type of the above mentioned PD antioxidants, is represented mainly by hindered amines and their derived products which are the most successful additives in the photo-antioxidant class, also known as HALS (hindered amine light stabilizers), and they are extensively tested and used in the modern polymer industry (*see for example*: Allen 1981, Allen *et al* 1981, Becker *et al* 1989, Chang and Chou 2000, Decker *et al* 1995, Decker and Zahouily 2002, Gijsman *et al* 1993, Gijsman 2002, Gugumus 1993, Gugumus 1995, Nicholson, 1991, Chirinos Padron 1990, Rytz *et al,* 1994). The hindered amines may act with two stabilizing mechanisms, as hydroperoxide decomposers and radical trappers (Allen 1981).

The basic structure of HALS is given in Figure 13.

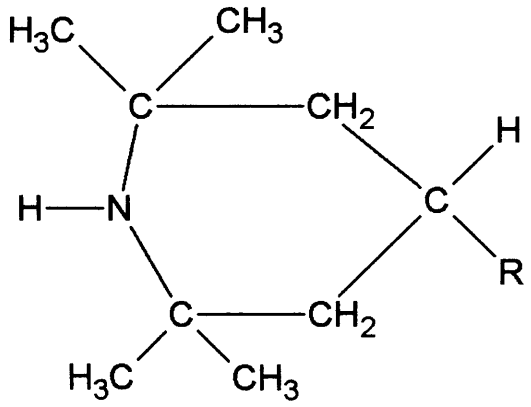


Figure 13. Basic structure of hindered amine (HALS) antioxidants

HALS is the only type of antioxidant that is believed to work entirely through an antioxidant mechanism. Unlike some other photo-antioxidants, hindered amines do not absorb any ultraviolet radiation and therefore they do not work as UV absorbers in any stage. Although HALS are primarily radical scavengers, the true antioxidants are their transformation products. These compounds work catalytically at some point and their transformation products are regenerated. This characteristic makes hindered amines more powerful than other PD-S antioxidants such as hindered phenols (De la Rie 1988, 15). It is also proved that HALS can also

protect many substances against thermal degradation and this is an extra advantage of this type (De la Rie 1988, Becker *et al* 1989).

HALS, as already mentioned, are the most widely tested and used antioxidants and they are presented as extremely effective free-radical scavengers and photodegradation inhibitors for plastics and coatings. The commercially available HALS are based on *2,2,6,6-tetramethylpiperidine*. A study by Bauer *et al* (1990) presents a variety of hindered amines belonging to this commercial type, and their performance as photodegradation inhibitors on acrylic melamine coatings. It has been noticed that the performance of the additives depends on the exposure conditions. This can be safely stated as the results, measured by infrared spectroscopy, vary between accelerated tests and exposure to sunlight.

Synthetic dyes and pigments are another area where HALS find application (*see for example*: Allen 1994, Jinjin and Grifiths 1991, Moura *et al* 1997). For example in a study by Jinjin and Griffiths (1991), a hindered amine antioxidant gave the best general results in the photostabilization of synthetic disperse dyes when tested in the form of ethyl acetate solution and cellulose acetate film. The authors therefore suggested that new extremely fast synthetic dyes can be prepared with the addition of HALS in the dye molecules and consequently used in the modern fabric industry. Allen (1994), in his study of the light stability of dyes and pigments used in polymers especially for outdoor uses, points out the satisfactory performance of hindered piperidine antioxidants although some anomalies are mentioned concerning specific pigments.

The review by Moura *et al* (1997) describes concisely the wider use of hindered amines in the modern polymer industry and their successful applications. For example: in disperse anthraquinone dyes, in epoxy resin films, in photochromic spirobenzoxazine dyes for automotive and building window materials, in dyed polyurethane fibres, in the construction of new lightfast dyes for automotive fabrics or even automotive clear coats.

In conservation, HALS were tested with success on picture varnishes and organic protective coatings (*see for example*: Decker and Zahouily 1998, Decker *et al* 1995, De la Rie 1988, De la Rie

and McGlinchey 1990a, De la Rie and McGlinchey 1990b, Potje 1984). De la Rie (1988), in his review of the use of photodegradation inhibitors in the conservation field, pays special attention to HALS by pointing out their complex function which is yet to be fully investigated. In his tests in the Metropolitan Museum of Art, HALS had the best performance on ketone resin and De la Rie believes that this type of antioxidant is the most promising for the conservation field. He also endorses the ability of HALS to protect against thermal degradation at room temperature, except light degradation.

4.3.c Excited State Quenchers

The last category of photodegradation inhibitors, the excited state quenchers, deals with the photo-excited molecules of the polymers themselves. If the excitation energy of the irradiated polymer molecules can be transferred to the additive and dissipated harmlessly as heat before any photochemical reactions can occur, photostabilization of the polymer will be successful (Wiles and Carlsson 1981, 67, Chirinos Padron 1989, 9).

Transfer of excitation energy can happen through collision of the polymer and quencher molecules (Lappin 1971). The success of the quenching procedure is dependent, therefore, on the collision of the polymer and stabilizer molecules. This will happen if the excited state of the polymer molecule is prolonged for a period. Unfortunately this does not happen with all types of polymers and the quenching mechanism is thus not always successful. It is also known that the concentration of the quencher must be comparable to that of the polymer in order to produce the necessary collision of the molecules (Lappin 1971, Randy and Rabek 1975). This is a disadvantage of this type of inhibitors.

The quenching mechanism can be explained through three main mechanisms:

Hydroperoxide quenching

This mechanism is theoretically based on the quenching of hydroperoxides. However, since peroxides and hydroperoxides are believed to undergo almost immediate photolysis when the polymer is irradiated with ultraviolet light, their quenching can be considered unimportant in practical systems.

Carbonyl quenching

This mechanism involves the quenching of excited states of carbonyl groups. There are several tested compounds that have been found to act as quenchers and many of them are effective photodegradation inhibitors. Among them are metal chelates, o-hydroxybenzophenones, hindered amines (HALS) and their derived products such as *nitroxyls* and *hydroxylamines.* On the other hand, as Chirinos Padron (1989) notes, *metal acetylacetonates* which are compounds belonging to the carbonyl quencher class, although proved to be successful carboxyl excited state quenchers, are also reported as severe photosensitizers of polymer photo-oxidation.

It is important to notice that the compounds mentioned before are also effective photodegradation inhibitors due to other mechanisms such as UV absorption (for the o-hydroxybenzophenones) and antioxidants (for hindered amines). As already explained, these compounds deal with the hydroperoxides which are the main initiators of polymer photo-oxidation and precursors of carboxyl groups. So, the role of excited state quenchers would be more important in the later stages of photodegradation when carbonyl groups are formed.

Singlet oxygen quenching

This mechanism is based on the quenching of the singlet excited state of oxygen. However, the concentrations of singlet oxygen in the atmosphere are usually very small and although, for example, some metal chelates have the ability to quench singlet oxygen, this does not correspond to their photostabilization efficiency (Chirinos Padron 1989, 11). Nevertheless, in several cases, it has been reported that singlet oxygen quenchers show a photostabilizing effect on dyes and their polymer substrate (Moura *et al* 1997, 180). In these cases too, one can suggest some other

mechanisms that work for the photo-stabilization of polymers. Examples are given by Moura *et al* (1997): nickel chelates can also act as radical scavengers, and tertiary amines can act as singlet oxygen quenchers and also interact with excited states.

4.4 Synergism of photodegradation inhibitors

In the early eighties and the nineties, twenty years after the introduction of inhibitors and their successful application in the polymer industry, the phenomenon of synergism between photodegradation inhibitors was reported by several researchers (*see for example*: Carr *et al* 1985, Chirinos Padron 1989, De la Rie 1988, Efimov *et al* 1983, Kikkawa 1995, Ivanov *et al* 1983, Reinert and Thommen, 1991, Shlyapintokh 1983, Vigo and Wyatt 1981). By synergism one means the ability of two additives, usually of different classes, to act together when mixed to achieve a better result than each of their two individual effects.

According to an early study by Shlyapintokh (1981), there are several mechanisms by which the synergistic phenomena can be explained in theory, but not all of them have been proved experimentally. Nevertheless, many scientists agree with his opinion, although the mechanisms of synergism are still not completely investigated (*see for example*: Chirinos Padron 1989, Efimov *et al* 1983, Ivanov 1983, Kikkawa 1995, Lozovskaya 1983).

The mechanisms of synergism between photodegradation inhibitors mainly involve the mixtures of the two main classes, the UV absorbers and antioxidants and can be summarized theoretically as follows:

- The first one concerns the mixture of UV absorbers with antioxidants reacting with free radicals. In this case, the two inhibitors do not react with each other, instead the antioxidant reacts with the peroxide radicals terminating the photo-oxidation reactions. If the UV absorber attenuates the intensity of light, which is absorbed by the polymer, the result will be fewer excited polymer molecules and less fewer peroxide radicals. This gives to the antioxidant the ability to work more efficiently.

- The second mechanism of synergism assumes that the absorber and the antioxidant inhibitors interact between them. During photoreactions, antioxidants may play the role of stabilizers, but they also act as photosensitizers. The action of a UV absorber in the mixture is the quenching of the excited states of the antioxidants. This results in improvement of the stabilizing function of the antioxidants. In addition, the initial excitation of the polymer is eliminated by the absorbing ability of the UV absorber. This mechanism can be applicable to the UV absorbers which act as excited state quenchers with both antioxidants reacting with free radicals and antioxidants which decompose hydroperoxides.
- A third theory for synergism suggests that with the addition of an absorber in the polymer composition, all incidental UV light can be absorbed by a thin surface layer of the polymer. In such case the deeper matrix layers of the polymer will be protected by the UV absorber as well as the added antioxidant. As the antioxidant will be consumed in the photoreaction zone, the concentration gradient of the antioxidant leads to its diffusion from the deeper layers to the surface of the irradiated polymer. In this way the photoreaction in the surface will be delayed for a longer period of time. This mechanism is usually referred to in the literature as the diffusion mechanism of synergism (*see also*: Chirinos Padron 1989, 32, Ivanov *et al* 1980, Ivanov *et al* 1983, 36 Shlyapintokh 1981, Shlyapintokh 1983, 1661).

In practice, synergism between known photodegradation inhibitors from different classes has been reported during several tests in polymeric materials. Synergism has also been observed between additives that have the same stabilization mechanisms, for example radical scavengers, such as hindered phenols and aromatic amines. The phenomenon is called *homosynergism* (De la Rie 1988, 16). Kikkawa (1995) and is also shown by hindered amines antioxidants (HALS) and phenolic antioxidants.

As already mentioned, the main examples of synergism are reported for UV absorbers and antioxidants but *heterosynergism* is also observed between aromatic amines and sulfides and between hindered phenols and sulfides (Pospisil 1984).

Successful combinations, as presented in the literature, are the mixtures of HALS and absorbers of benzophenone and benzotriazole types (*see for example*: Allen *et al* 1989, Chirinos Padron 1990, De la Rie 1988). Ivanov *et al* (1982) also report the successful mixtures of *2(-2-hydroxy-5-methylphenyl)benzotriazole* and nickel or zinc dialkydithiocarbamates. Scott and Yosoff (1980) discuss the synergism between the UV absorber (*2-hydroxy-4-octoxybenzophenone)* and phenolic antioxidants when tested on polypropylene. Chakraborty and Scott (1977) report that *2-hydroxy-4-octyloxy benzophenones* synergize perfectly with metal dithiocarbamates (antioxidants) and hindered phenols.

However it is not rare for an antagonistic effect to be reported. This means that the mixing of additives gives *worse* results. For example, the interaction of hindered amines with metal complexes can be either synergistic or antagonistic and it seems that the phenomenon is dependent on the chemical structure of the polymer, the concentration ratio and the method used to investigate the interaction (Chirinos Padron 1990, 143). Also, hindered phenols and metal dithiocarbamates are reported to act antagonistically when mixed during photo-oxidation while they synergize effectively during thermal oxidation (Chakraborty and Scott 1977). Antagonistic effects are also reported by several scientists in mixtures of HALS and organic phospites and HALS and sulphur-containing antioxidants, as presented in a review by Chirinos Padron (1990).

Another view of synergism is presented by the same author (Chirinos Padron 1989) regarding mixtures of thermal antioxidants and photo-antioxidants, in the case where the polymer needs to be exposed to solar radiation, and ultraviolet as well as infrared light is under consideration. In such cases, synergism is reported between the two additives. Synergistic effects are also presented in mixtures of UV absorbers with thermal antioxidants in the above mentioned conditions, because the absorber protects the antioxidant from photolysis by inhibiting

the penetration of radiation into the polymer. The antioxidant on the other hand, protects the UV absorber from being consumed, by inhibiting its reaction with radicals (Chakraborty and Scott 1977, Shlyapintokh 1983).

Testing of synergistic effects on textile fibres is very limited. Reinert and Thommen (1991) present in their paper the photostabilization of polyester and polyamide fibres and report a synergistic effect between a UV absorber and a copper complex which gave physical as well as chemical protection to the newly produced fibres. Carr *et al* (1985) tested several mixtures of commercial UV absorbers and antioxidants on wool and only hindered phenols in combination with absorbers gave useful synergistic effects.

4.5 Degradation of Photodegradation Inhibitors

Photodegradation inhibitors may be photodegraded themselves. The photodegradation of ultraviolet absorbers is the more extensively studied as it is noticed that after some time of exposure, the additives lose their ability to absorb radiation (Allen *et al* 1981, Bell *et al*, 1993, Picket and Moore, 1995, Picket, 1997).

A typical way for loss of effectiveness of a UV absorber is physical loss through migration, volatility or extraction. A second way may be the interaction of the additive with the photo-oxidation products of the substrate, such as radicals and peroxides (Allen *et al* 1981). It is important to notice that in the presence of antioxidants, such as hindered amines, which stabilise the substrate polymer, the rate of degradation of the absorbers is much lower (Bell *et al* 1993). This is also a beneficial result of the synergism of stabilizers, discussed above.

The degradation of UV absorbers is also noticed in oxidizing environments, meaning that the additive may react with chemically hostile environments. A third possible way for absorber degradation is photochemical behaviour in which the internal hydrogen bonds are weakened (Picket 1997, 128). In this case the hydrogen transfer, which deactivates the excited states, is

difficult and the excitation times are longer. This makes the absorber's anion susceptible to photolysis and oxidative destruction.

In practice, all of these three possibilities may happen at the same time to result in degradation of the additive after prolonged exposure to electromagnetic radiation. Picket (1997) presents an estimate of the quantum yield of the most important classes of UV absorbers, of the order of 1×10^{-6}, when tested on films and coatings in accelerated tests and outdoor exposure.

4.6 Application of photodegradation inhibitors to fibres

The method of application of photodegradation inhibitors to the textile surface has proved to be extremely important and to have a strong bearing on the effectiveness of the inhibitors.

Most researchers prefer to treat fabrics by placing them into baths of the dissolved substance (*see for example*: Becker *et al* 1989, Carr *et al* 1985, Cegarra and Ribe 1972, Crews- Cox, 1984, Evans and Waters 1981, Leaver 1982, Riedel and Hocker 1996, Waters *et al* 1980, Waters and Evans 1981). The selection of solvent is also an issue, as water-insoluble absorbers sometimes are unable to produce a uniform deposition on the surface of the fibres. It is well known that water swells the fibre much more than organic solvents and the use of water in the solutions will result in a better introduction of the inhibitor within the fibre. Rose *et al* (1961) reported that the application of water-soluble benzophenone sulfonates on wool proved to be effective against yellowing. This can be explained theoretically as the ultraviolet absorbers have some chemical groupings suitably arranged to match with some reactive and sensitive parts in the wool protein. According to this theory, the aqueous solution penetrates the fibre and helps the inhibitor to reach these reactive sites (Rose et al, 1961).

On the other hand, others believe that the non- aqueous inhibitors have better results in the protection of natural fibres. The fact is that not all types of fibres react in the same way to similar additives. For example, as mentioned above, the water-soluble absorbers can be suitable for undyed and non mordanted wool, as they protect from yellowing; but in the case of linen and

silk they seem to be less effective, as they have proved to increase the colour change (yellowing) and the degradation of the fibres. Furthermore, it is reported that the non- aqueous inhibitors showed better protection against yellowing in cotton, linen and silk fabric than the water-soluble ones. As for the dyed and mordanted wool materials, it is reported that mostly the non- aqueous photodegradation inhibitors can be helpful, as in some cases the water soluble ones caused more photodegradation on fibres than photoprotection (Crews-Cox, 1984).

The method of application by solution of the additive, whether water soluble or dissolved in a non- aqueous solvent, is firstly the simple soaking of the fibres in the solution (*see for example*: Becker et al 1989, 98-99, Evans and Waters 1981, 432, Riedel and Hocker 1996, 685) and sometimes the increase of temperature and the addition of dye additives, usually acids, in order to simulate the dyeing procedure, when the application is done through an aqueous solution. Leaver (1982), for example, applied a benzotriazole inhibitor to already bleached wool through a water solution with the addition of sulfuric acid and sodium sulfate[18], and he raised the temperature to 60ºC during the application procedure. Ceggara and Ribe (1972) treated wool fabric with a benzophenone inhibitor in higher temperatures of 100°C.

Many researchers prefer to apply inhibitors to fibres with the use of dyeing machines used in the fabric industry, usually with the addition of dye additives following a classic modern dyeing procedure. Carr *et al* (1985), for example, applied a sulfonated benzotriazole inhibitor to wool using a dyeing machine with the addition of sodium sulfate and sulfuric acid at a higher temperature of 80ºC. The same researchers also applied a solvent soluble inhibitor with a relevant dyeing procedure, using aqueous dispersions of the inhibitor in the presence of a dispersing agent and an even higher temperature of 100°C (*see also*: Riedel and Hocker 1996, 686, Waters and Evans 1983, 99, Waters *et al* 1980, 197). Finally, there are cases where a padding machine is

[18] Usual dye additives for acid dyes. They help the absorption of dyestuff by the fibres, by minimizing the repulsive forces operating between the dye molecules and the fibres (Textile Conservation Centre Notes, 2001)

used in order to remove mechanically the excess inhibitor solution from the fabric samples (*see for example*: Becker et al 1989, 99, Riedel and Hocker 1996, 685).

Another method suggested for the application of photodegradation inhibitors is that of evaporation impregnation, during which the stabilizer tends to form an external coating on the surface of the fibre (Head and Lund 1969, 62). In this way, best protection could be achieved if the photodegradation mechanism depended on a simple screening action (Rose *et al* 1961). It has to be mentioned at this point, that in many cases some substances proved to absorb highly in the ultraviolet and yet seem to offer no satisfying protection to the yellowing of the fibres caused by light. This means that the protection obtained from the additives is not only a result of a simple light screening but also a result of other factors involved.

Finally, a last suggestion for the application of inhibitors is to merge the absorber in resin latex and apply it to the fibre surface. Since the fibre and the latex polymer have equal densities, a film of 0.25μ can be prepared on the basis of 5% latex solids and applied uniformly on the surface. Still, the absorbing ability of the coating reduces if it becomes thinner, so the amount of ultraviolet radiation absorbed will be small if the film is thin which could be the case for aesthetic reasons (Gantz and Sumner, 1957). Therefore the application of inhibitors using this method is not a good solution in the case of textile fibres as this will affect the texture and flexibility of the fibres.

Section summary

Photodegradation inhibitors are materials used in the modern polymer industry as additives in the production of polymeric materials, plastics, coatings, varnishes, synthetic fabrics and synthetic dyes with increased light fastness.

According to their mechanism of photostabilization, inhibitors can be classified into three major groups, the UV absorbers, the antioxidants and the excited state quenchers. From the three classes, the most widely used and tested in polymers in general, and more specifically in textile fibres, are absorbers and antioxidants. Synergistic effects are also observed between them.

Commercial photodegradation inhibitors used in polymer manufacturing, although proved to be a very effective tool for the life prolongation of polymers, are photodegraded themselves with no thoroughly investigated mechanisms and results.

The application methods used for textile materials simulate dyeing and finishing procedures which sometimes include the use of specialized industrial equipment.

The possible use of these additives on historic textile objects can be considered only under the strict prerequisites of textile conservation practice and ethics.

5. Photodegradation Inhibitors and Textile Conservation

As presented in the above review, the use of photodegradation inhibitors for the photostabilization of polymers is a common practice and there have been several attempts to use them in the production of new fabrics with increased light-fastness. The application methods are combined with dyeing or finishing procedures in the production of textiles, or may even entail the introduction of the additives into the chemical structure of new synthetic fibres or the backbone of new synthetic dyestuffs.

Approaching the subject from a conservation point of view is different. There are several necessary limitations as far as historical or art objects are concerned. The addition of photodegradation inhibitors to varnishes and coatings for objects of art is a good starting point but still the additives are included in a medium (varnish or coating) and then applied to the object's surface. In the case of museum textiles the requirements are much more restrictive as the additives would be absorbed by the fibres which are the main structural material of the object. The substrate (the textile) is already degraded and delicate and the method of application should be appropriate without putting the object at risk. Textiles are complex and may sometimes include other materials as decoration or structural units that may be influenced negatively by the application. The issue of reversibility of treatment is also a topic to be addressed, as well as the long term effects of the additives on fibres, dyes and other

construction materials. The main points of discussion on the use of photodegradation inhibitors in textile conservation are given below and they constitute the basic values under consideration during the planning of this research:

5.1 Suitability for use on historic textiles as a conservation treatment

In order for a photodegradation inhibitor to be suitable for application as a conservation treatment to historic textile materials, it must satisfy the following requirements:

- ✓ *It must be colourless,* meaning that it should transmit all radiation of the visible region of the spectrum, a fact that makes it transparent. It should not change the hue or depth of colour of a dyed textile and this characteristic must stay unchanged with the passing of the time, even if the effectiveness of the additive is diminished because of ageing.
- ✓ *It must not affect the texture of the substrate* (the fibres), or interact with the textile material in any harmful way. One of the most important attributes of textiles is their flexibility and this characteristic is usually at risk when added materials are introduced into the fibres. The change of flexibility may be a deliberate action in the production of new fabrics with the addition of finishes, but it is also an undesirable effect from the addition of consolidants or adhesives in conservation of archaeological or historic textile objects. The application of photodegradation inhibitors should not affect this quality of historic textiles, not only at the time of application but also after ageing.
- ✓ *It must not change the mechanical properties of the fibres* such as the tensile strength and elongation after the application, but also after ageing. It has to be mentioned that these two properties diminish if the textile is photodegraded and an

effective inhibitor should also be expected to protect the fibres from this risk. Furthermore it is essential to bear in mind that the mechanical properties of historic textiles are usually already affected due to natural ageing, and the application of inhibitors should not aggravate their condition.

- ✓ *It should not interact with or be affected by the complexity of construction materials* or techniques present in the same object, such as different types of fibres and dye mixtures or complex weaves and embroideries. Its performance should be beneficial to some extent to all the components of a textile object.
- ✓ *It should not affect negatively in any way other construction materials.* As museum textiles are not only made of natural fibres but are most of the time ornamented with a series of other added materials, such as dyes and pigments, metallic fibres, precious stones, glass beads, leather or paper, any additive should not affect these materials too. A common example of this is the use of water in textile conservation, which is very often restricted because although it is beneficial for the cleaning of textile fibres, it may destroy the applied decoration of the object. Having this in mind, the use of photodegradation inhibitors on historic textiles should be appropriately tested not to affect any of the other construction materials of the objects, even if it is considered of assistance to the textile substrate.
- ✓ Finally, as the intention of conservation is to achieve the life prolongation of art objects for so long as possible, any added materials should be stable and effective throughout the object's life. If this is not the case, the degradation of the additives should not affect negatively the structural materials of the objects. As far as photodegradation inhibitors are concerned when used on historic textiles, they should

be stable upon ageing and their possible degradation should not affect the textile. As Lappin (1971) states:

> *"An effective stabilizer must dispose of its excitation energy without interacting with the polymer in harmful ways and without undergoing any photochemical reaction which would destroy its effectiveness".*

5.2 Method of application for textile conservation

Another important factor in the use of inhibitors in textile conservation is the method of application. As these materials are expected to be used in a conservation laboratory and on objects of historic value, several rules apply. To be acceptable for textile conservation purposes, an inhibitor must:

- ✓ be soluble in acceptable solvents for textile conservation, as used in other procedures like wet or dry cleaning, whilst also not affecting the fibres or dyes. Therefore high temperatures are not permissible. At the same time, the inhibitors must not interact with the solvent and must remain unchanged, in order to maintain their stabilizing characteristics.
- ✓ When in solution the pH must also be considered, as acidic solutions will cause irreversible damage to fibres (Landi 1985, Timar-Balasky and Eastop 1998).
- ✓ When in solution the selected methods of application must be delicate to the fragile textile but also suitable for the essential distribution of the inhibitor in the fibres so as to be effective. The inhibitor solution must uniformly absorbed by the textile without causing spots, marks or other visual imperfections.

- ✓ It must not be toxic or dangerous to human health because it will be used in a conservation laboratory in everyday context, and its commercial form should be handy and usable.
- ✓ It must be easily removable from the textile, using simple, non-destructive, cleaning techniques. This is because any material added to historic or archaeological objects may interfere with future analytical work, or a new and better treatment may be discovered and need to be applied.

5.3 Reversibility of additives

Based on the last mentioned requirement, the issue of reversibility of additives must be discussed briefly at this point.

The decision to add new material to historic or archaeological objects has a long and controversial history. Ideally, in order for a material to be chosen for use during a conservation treatment it should not cause any changes to the object during its complete cycle of application, ageing and removal (Horie 1987, 6). Conservators for many years during their education but also during their professional life know that reversibility is the basic ethical goal for every treatment (Charteris 1999, 141, Barclay 1999, 157). However, the meaning of the term "reversible" is questionable in applied conservation and one should give more attention to the context of this word when making decisions in conservation practice (Oddy 1999, 1).

By the term reversibility conservators refer to the potential of removing any material or reverse the effect introduced to an object by a conservation treatment. This should be the case both at the time of the application and more importantly after aging. Ideally a conservator would like to have the ability to return any object to its original stage before any conservation

treatment occurred, any time she/he wants or she/he is asked to, without causing further damage to the object (Smith 1999, 99). In fact the whole idea is much more complicated than this, because it is clearly proved by chemical thermodynamics that reversibility does not exist in nature and will never do (Palazzi 1999, 175, Seely 1999, 162).

The basic problems of reversibility in conservation context are the impossibility of its realization and the austerity of the term which allows no qualification (Barclay 1999 ,157). Although many conservators in the past have tried to reverse previous conservation treatments, they have never succeeded to ensure complete removal. Therefore, frequently, in conservation reports and papers it is mentioned that a material or a treatment is "not reversible" or "very reversible" or even "almost reversible" trying to explain the amount of their success which is of course not complete. From the above it can be understood that, as far as the addition of new materials as conservation treatments concerns, the question of their removal is of primary importance. Removal is an action that can have several degrees and can be measured even with scientific methods (Barclay 1999, 159). Therefore if a photodegradation inhibitor is selected to be used to an historic textile, its removability should be checked more preferably after ageing. The degree of removal of the additive, the method needed to do so, and the prospective damage caused to the object by this action are the points to be evaluated.

All conservation treatments may cause damage, and if new materials are added they will surely leave residues, even small, and this cannot be avoided or completely removed (Smith 1999, 100). So the fundamental issue is the understanding of the ageing characteristics of the materials used (Pavelka 1999, 105) and their behaviour in the future in accordance to the object it is applied to. Having in mind that an inhibitor would never be totally removed from a

textile, but still it is judged beneficial to the improvement of its light stability, it is important to predict its performance after ageing and possible negative effects on the textile components.

According to this value, the whole idea of reversible treatments over the years helped conservators to minimize unserviceable treatments, especially in restoration work, and make them more responsible in choosing the correct materials and methods of application. But also, the idea of reversibility made some people critical to any interventive treatment and any new material introduced (Palazzi 1999, 177). In this way no conservator wants to put him/herself to criticism to decide for a new treatment and this attitude is capable of stopping further evaluation of a promising new treatment (Smith 1999, 101). Of course this does not mean that it is acceptable to treat any object with any material. On the contrary, all interventive treatments should be considered, thoroughly tested and justified before chosen to be applied to an object, but it has to be understood that most treatments are not and cannot ever be reversible (Oddy 1999, 3).

As far as photodegradation inhibitors tested in this research are concerned, under conservation requirements, consideration of their removability from treated textiles is essential, and must be considered as one of the important factors relating to their suitability for museum textiles.

6. The Present Study

6.1 Aim and Objectives

Having reviewed the available literature on photodegradation inhibitors and their use in the modern polymer industry, and having in mind the needs and restrictions determined by the conservation of historic textiles, the aim of this research is to evaluate the possible use of photodegradation inhibitors as a conservation treatment for historic silks. This was based on the literature review on a) the function and use of these inhibitors in modern industry for textile applications (*see Chapter 4*), and b) the conservation requirements for the use of new materials and ethics (*see Chapter 5*). So the main question to be answered from this study is: *Can photodegradation inhibitors be used successfully in textile conservation?*

The objectives therefore, which would lead to the answer of this question, are given as follows:

- ✓ *To base the experimental work on original silk textile objects* trying to investigate further the complicated problems they present. The identification of original historic samples showed that hardly any historic textile was dyed with one dyestuff only. Instead mixtures of dyes were used in order to create the desirable colour *(see Chapter 7)*.
- ✓ *To select commercial photodegradation inhibitors that satisfy conservation requirements.* Additives were selected through preliminary tests and market research having in mind

criteria such as colour, solubility, toxicity, ease of application, removability, according to textile conservation practice (*see Chapter 8*).

- ✓ *To evaluate the action of selected photodegradation inhibitors on the textile substrate.* Possible changes of colour or mechanical properties were investigated and evaluated according to conservation requirements (*see Chapter 9).*
- ✓ *To evaluate the ability of the selected inhibitors to increase the light fastness of silk dyed with red dyestuffs and dye combinations.* Textile samples treated with inhibitors were artificially aged in different lighting, temperature and humidity conditions simulating possible degradation observed in historic textile objects (*see Chapter* 10).
- ✓ *To investigate if there is a synergistic effect of some inhibitors.* Mixtures of commercial photodegradation inhibitors were applied to the samples and evaluated for better or worse photostabilization results (*see Chapter 9 and 10*).
- ✓ *To evaluate the suitability of the selected inhibitors for use in textile conservation as an interventive stabilization treatment.* Having in mind not only the effectiveness of the additives in extreme artificial ageing tests, but with the sensitivity of a textile conservator dealing with an already degraded and unique object, the evaluation of the selected additives was addressed from a different point of view than any former research on this topic (*see Chapter 9 and 11*).
- ✓ *To appraise the impression caused by the use of these materials, according to present conservation practice and ethics.* Ethical issues of conservation in the use of photodegradation inhibitors on historic textile objects are discussed in association with professional conservators' opinions (*see Chapter 11*).

6.2 Design and methodology

This study is divided into three parts. The first part involves the selection and identification of original samples coming from historic textile objects already showing photodegradation. This helped the investigation and understanding of the problems facing historic textiles in the museum context.

The second part involves: a) the production of new sampling material, with traditional dyeing techniques, simulating as far as possible the original samples b) the selection and application of inhibitors and c) the evaluation of treatments as far as conservation restrictions are concerned.

The third part is dedicated to light fading tests of the textile samples treated with inhibitors and the evaluation of their performance in improving photostability.

The first part of this study is divided into the following stages:

Tracing of the problem. Photodegradation of textiles is a major and unsolved problem *(see Chapter 2)* and dependent on many parameters (type of fibres, dyes, environmental conditions). It was necessary therefore to focus this research by limiting the parameters in order to achieve a more detailed approach on the selected ones. With this in mind it was decided to review the current trends. A questionnaire was compiled and sent to museum professionals around the UK asking them to share their observations and problems faced in their collections *(see Appendix D.2)*. This questionnaire consisted of 26 questions and was addressed not only to conservators but also people working with textiles in the museum context (*see Appendix D1*). It was focused on their macroscopic observations on the objects and personal experience, related to photodegradation, regardless their specialization. The response to this questionnaire significantly contributed to the methodology of this research.

Selection of historic samples. Samples from Greek historic textiles were selected, because textiles of east Mediterranean origin are subject to severe photodegradation, due to the area's environmental conditions (intense sunlight). From the available objects, silk fibres were selected dyed in red shades. The preference for silk was also activated by the sensitivity of silk to photodegradation *(see also section 2.1.b),* its wide use in historic textiles and especially ecclesiastical vestments and limited testing with inhibitors in modern industry *(see Chapter 4).* The preference for red dyes arose from the rich literature and frequency in use of these dyes on historic textile objects.

Identification of construction materials in historic samples. Several identification techniques were investigated and finally some were applied to the selected samples for positive identification of fibres, mordants and dyes. The scope of this action was firstly to appraise the complexity posed by historic textiles as far as materials and techniques used for their construction are concerned, as well as the induced degradation which is evident in every historic object. Using some representative results of this identification, new sampling material was prepared in order to base the experimental work on realistic conditions.

The second part of the methodology of this research is structured as follows:

Selection and preparation of the new samples. New samples were prepared using silk fabric and threads and dyed with natural red dyestuffs and dye combinations previously identified on historic samples, with traditional dyeing methods *(see sections 8.1and 8.2).*

Investigation of authenticity of the new sampling material. The newly selected and prepared fabric and thread samples were investigated using instrumental analytical techniques in order to confirm their validity (*see sections 8.1.a and 8.2.b).*

The application of inhibitors. Commercial photodegradation inhibitors selected through preliminary testing and conservation restrictions were applied to the newly prepared samples *(see section 8.3 and 8.5).*

Evaluation of treatments. The inhibitors were evaluated with regard to conservation requirements by means of solubility in different solvents, induced colour changes, changes of mechanical properties of fibres and removability *(see Chapter 9).*

Finally the third part includes the following stages:

Exposure to light. Four artificial ageing tests involving exposure of the samples to radiation were applied in order to evaluate the ability of inhibitors to increase the lightfastness of silk fibres and dyes. These tests were selected gradually according to the observed results and are based on international standards, different times of exposure, high temperature and different levels of humidity *(see Chapter 10).*

Evaluation of the results was done by microscopic and colourimetric techniques. Much consideration was also given to conservation ethics discussed in association with the current users' (conservators) opinions *(see section 11.4).* This was supported by a second questionnaire which was compiled after the first results of this research and sent out to museums having textile collections in Britain and Greece, where the original samples came from. The questionnaire consisted of ten questions attracting at first information about the existing preventive conservation methods in each museum and how sufficient they have proved to be against photodegradation. Following that, information on the inhibitors and their performance was given gradually in order to see the reaction of each conservator to the idea of using such materials on textiles. The method of application and the solvent used was also discussed (*see Appendix D3*).

6.3 What this research is not about

The main compromise of this research is the textile samples which, although specially prepared to simulate historic textiles, come from contemporary materials and have not therefore undergone prior degradation. Historic textiles displayed in museums and subject to photodegradation are already degraded and soiled, and their degradation products as well as other added materials (finishes, former treatments, soiling) may affect their lighfastness as well as a photo-inhibitors' performance. It was decided within the framework of this research not to test the performance and applicability of the additives on original and already degraded textile objects. The choice of predefined sampling material helped in the isolation of the problems and the defined evaluation of the results.

Also, historic textiles are complicated objects and usually their construction characteristics involve the use of fibres of different origin, mixtures of dyes, complex weaves and applied decoration with other materials such as metals, stones, pigments, paper and other organics (e.g. pearls, ivory) which may either affect the lightfastness or be affected by the application of inhibitors. From all these factors, only dye mixtures were examined in the present research with the hope of opening a new field of research including a series of tests involving other parameters *(see Chapter 12).*

Another limitation of this research was the use of artificial ageing tests which, as commonly known, can never simulate real conditions. As mentioned before, the main radiation source is the sun and the sunlight reaching the earth's surface is limited, for several reasons, between certain wavelengths. On the other hand, museum textiles are exposed to particular wavelengths, according to the preventive conservation measures taken. Therefore not all textiles displayed in every museum are irradiated with exactly the same radiation. In the present research, under these limitations and the available equipment it was necessary to choose a

certain scheme in order to expose the treated samples in a controlled manner. That is why an artificial light source imitating the sunlight passing through an ordinary window glass was chosen as a concession. UV filtering of light sources during artificial ageing was not included in the present research, although is a common practice in modern museums, because the intention was to simulate non-ideal museum conditions such as the ones found in small museums, open and folk art collections and touring exhibitions.

The use of accelerating aging tests to evaluate the performance of materials through time has a long and controversial history. As stated by many scientists, it is impossible to predict the behavior of a material through time under expected conditions of use, as the conditions cannot be rigorously reproduced and accelerated. Nevertheless, accelerating aging is an important tool in conservation science, because it is unacceptable to apply new materials to historic objects without prior testing on sacrificial materials in controlled and measurable conditions.

Finally, photodegradation of historic textiles is not only a matter of fading, as many other changes are induced and other parameters can be measured. For example, changes in the mechanical properties of the fibres, and chemical changes in the fibre polymer and dye molecules can be estimated and possibly measured with analytical techniques. The present research is intentionally focused mainly on visual changes, such as the microscopic appearance of the fibres and colour changes of the dyes, although measurements of tensile strength are also presented.

It is hoped that this study will open a new field of research in conservation science for historic textiles and the still unsolved problem of photodegradation. It will not necessarily propose the addition of photo-inhibitors to every textile object subject to light degradation, but it is hoped that scientists and conservators will be made aware of the possibilities for collaboration in this area.

7. Historic Samples – Collection and Identification

7.1 Collection of historic samples

One of the primary aims of this research was to base the experimental work on conditions that are as realistic as possible to the problems conservators and curators are facing with historic textiles. That is why the methodology of the experimental procedure started with the collection and identification of samples from historic textiles. The analysis and identification of these samples gave information on the type of fibres, mordants and dyes used. This information was used later on, in order to prepare new sampling material, as similar as possible to the original. In this way the sampling material was unlimited and enough to do as many tests as were needed to evaluate the suitability and effectiveness of the inhibitors. Also, by preparing new material similar to the old one, one is dealing more with the reality of the problems that historic textiles are facing. As already mentioned, the dyestuffs and dye combinations used as well as the selected mordant are factors affecting the light fastness and in the case of historic textiles the situation is always more complicated. Until now the stabilizing effect of any inhibitor was isolated to one dyestuff at a time and this is not what one usually finds in a historic textile as proved later on.

7.1.a Origin of the historic samples

All original samples used in this research were collected from Greek museums in Athens that own and display textile collections: the Museum of Greek Folk Art, the Byzantine and Christian Museum of Athens and the Benaki Museum.

The Museum of Greek Folk Art has one of the richest historic textile collections from 16th to 20th century in Greece, consisting of traditional costumes, embroideries and decorative art textile objects from all over the country. The Museum belongs to the state and is under the Ministry of Culture. Founded in 1918 , it was firstly housed in a "tsami"(Ottoman temple) and the collection was in display in this building until 1973, when it was transferred to another more modern building in Plaka, at the centre of Athens. Records of the condition of the objects as well as display conditions in the first building were not kept. Its traditional embroidery and costume collection is considered to be the richest in Greece and it was the first Greek museum to establish a textile conservation laboratory[19].

The Byzantine and Christian Museum of Athens is also a state museum, belonging to the Ministry of Culture. It has one of the richest collections of Byzantine and post Byzantine textiles, sacerdotal vestments and ecclesiastical textiles from 11th to 19th century. It was founded in 1914 and it has been housed in the "Ilisia" mansion since 1930, in the centre of Athens. The mansion is a building of 1848 and belonged to the Duchess of Placendia. In recent years, a large extension of the museum was built in the form of basements and buildings in part above ground. The Byzantine and Christian Museum has owned conservation laboratories since the 1960s, which at that time covered the needs of the whole country, as far as icon conservation was concerned. However, textile conservation was introduced to the museum in the mid-nineties. No records of the former condition of textile objects or display conditions are kept[20].

The Benaki Museum is a private museum based on the private collection of one of the richest Athenians, E. Benakis, born in Alexandria in 1873, and enriched after his death by

[19]more information on the museum and its collections can be found at web site: www.culture.gr

[20] more information on the museum and its collections can be found at web site: www.culture.gr

donors and new purchases. Benakis began his collection in Alexandria and donated the collection to the Greek state after his settlement in Athens in 1926. The main building of the museum, where the collection was first housed, is the actual house of the collector, a neoclassical building in the historic centre of the city, opposite the National Gardens and the Presidential Palace. It holds a large collection of textiles from antiquity (Egyptian, Coptic and Islamic) but also has a very important collection of folk art costumes and furnishing textiles from 1453 (the fall of the Byzantine Empire), to the 19th century, as well as ecclesiastical vestments and ceremonial textiles from the 16th century (when the Orthodox Church began recovering from the Ottoman conquest) to the start of 20th century. The museum has a well equipped textile conservation laboratory, among others, which is also relatively newly established and no sufficient records of the former condition of the objects are available[21].

7.1.b Sampling procedure

The criteria for selecting samples from historic objects from the three above mentioned museums were as follows:

According to the selected methodology of this research, sampling was performed only on objects containing fibres dyed in red shades. This decision was taken quite early as it was soon realized that the complexity of the problems involving different coloured dyes on historic textiles would be non-confrontable within the limits of this research. The selected samples therefore were easily identified by macroscopic investigation during a visit to each collection.

The second criterion was to choose samples of silk fibres only. The selection of samples from silk objects and embroideries made by silk threads was done using macroscopic methods, historical information on the selected objects and the advice of the

[21] more information on the museum and its collections can be found at web site: www.benaki.gr

responsible curator or conservator of each collection. This choice was confirmed with fibre identification methods later.

The last consideration on the choosing of sampling material was to cover as many historic periods as possible and different locations around Greece, in order to investigate possible changes in technology through time and differences in deterioration of the objects. Under this scheme samples were taken from objects dated from 16th to 19th century originating from different parts of the country.

The samples included silk threads from embroideries as well as pieces of silk fabric. The sampling procedure was done under conservation restrictions and with the supervision and help of the museum conservator. For every sample taken a specially made record card (*see Appendix A, section A1)* was filled with information not only for the sample but for the whole object too and any conservation treatment it had received. This information proved helpful afterwards for the positive identification of fibres and dyes.

The sampling procedure was performed very carefully, by cutting away tiny pieces of material from degraded parts and irregularities in the case of embroideries. The general principle when sampling is to try to have enough samples to examine conveniently and yet representative of the original material (Wildman 1954). Still, when sampling is performed on historic textile materials one is guided more on what the object itself wants to give. From the textile pieces, which form the background of embroideries made with gold and silver threads, small parts were cut away from the frayed edges or mechanically damaged areas, without damaging the object. From each object two samples were detached where possible, one from the front and one from the back side in order to investigate any changes caused by light on the most exposed front side of the object. More detailed information for each sample taken can be found in Table 7 that follows.

The area where each sample was taken was measured by tristimulus colour measurements with the use of a Minolta CR-221 chromameter with light source C, a 3mm diameter measuring area, and a 45° illumination angle. The meter was calibrated before each measuring session using standard white plate. For each sampling area selected three measurements were taken. The whole procedure is non destructive to the object. These measurements were used later for comparison with newly prepared samples.

Table 7. Fibre samples taken from historic textiles belonging to Greek museums in Athens and selected for further investigation

Museum	Object no	Object type	Cat. no	Date/ century	Origin	Historical Information	Conservation treatment
Museum of Folk Art	1	Shirt border	50	18th	Crete	This piece of clothing was used as a petticoat under special occasion clothing such as bridal costumes. The fabric used is white linen embroidered with silk threads. The stitches employed in Cretan embroideries are the ones used in Byzantine ecclesiastical embroidery. The shades of colour used in the motifs which vary, from a single red blue colour to multi coloured silks in bright shades, come close to the colour and the richness of Italian Renaissance silk embroideries. The piece is a part of the collection since 1920	Washing with deionised water and anionic detergent
	2	Shirt border	51	18th	Crete	Same construction and use as the sample no1	-
	3	Bed sheet border	643	18th	Cyclades island	*Bedsheet border* depicting a wedding procession scene on a drawn threadwork ground. It is part of the collection since 1921. It is made of linen background embroidered with silk threads and it a was decorative object in everyday use.	Washing with deionised water and anionic detergent
	4	Bed spread	3129	18th-19th	Naxos island	Linen *bed spread* embroidered all over in red silk thread. It was an everyday use decorative object from Naxos, Cyclades islands, representing a network of stylized leaves and its is a part of the collection since 1964	washing with deionised water and anionic detergent, couching and supported with a new fabric at the back in deteriorated areas
	5	towel	15	18th	Cyclades islands	It is made of an embroidered linen with silk threads and it is one of the oldest pieces of the collection, since 1919 when the museum was called the Museum of Decorative Art	Washing with deionised water and anionic detergent soap
Museum of Folk Art	6	Bridal bed sheet	3518	Late 18th	Ioannina	*Bridal bed sheet* with dense embroidered ornamentation with the pinecone motif. It is originating from Ioannina in Epirus and it is made of embroidered linen with silk. It is only used once and it was very preciously kept afterwards as it was the evidence of the virginity of the bride	-

Museum	Object no	Object type	Cat. no	Date/ century	Origin	Historical Information	Conservation treatment
Museum of Folk Art	7	Epitafios	1766	1620	Asia Minor	Three samples were taken from different parts of this object having different red shades. The object is an *epitafios*, which is an ecclesiastical piece of embroidery made of silk, gold and silver threads on a silk background. The piece is coming from Asia Minor and it is signed with the date 1620. It is a very important ceremonial object, used once a year in the Orthodox Easter period. It is part of the collection since 1970 and it is not displayed yet as it is in a very bad and delicate condition.	Under conservation treatment during sampling procedure
	8	Sperveri	-	18th	Rhodes	Sperveria were long curtains that adorn and isolate the bed from the rest of the house. Their stylized decoration and chromatic unity characterize the embroideries of the Greek Aegean islands. The most beautiful examples of these embroideries are the red sperveria (bed tents) and sheets, the entire surface of which is worked in vertical rows. This door was made of embroidered linen with silk threads.	-
Byzantine museum	9	Epigonatio	T.1024 X.A.E 5002	16th	Florence	It is a sacerdotal vestment, a small rectangular piece of cloth usually hanged from the belt of the archpriest. It made of silk satin fabric painted on the top with different pigments.	-
Bekani museum	10	Epimanikio	34218	19th	-	Epimanikio was the cuff worn by the clerics of the Greek Orthodox Church. Pearls, gold and silver wires are worked with silk thread in a silk ground. The usual subject depicted is that of the Annunciation, with the Virgin embroidered on one cuff and the Angel on the other, among floral scrolls. In this case the Virgin with the Child is seen	The object was under conservation treatment in the time of the sampling procedure
	11	Epimanikio	34221	19th	-	*Epimanikio* of the same date and nature as the previous one. In this case the embroidered gold threads on silk ground represent the Annunciation.	The object was under conservation treatment in the time of the sampling procedure

7.2 Fibre Identification methods

Several methods are used to identify fibres and to differentiate them from one another. Therefore the selection of the method or methods in order to investigate the types of fibres in the selected samples was dependent on different parameters. After reviewing the available literature, the decision was made in consideration of the size of the available samples, the equipment available, the prospective information and its usefulness. The most common methods are reviewed next and include solubility tests, heating and burning characteristics, staining techniques, microscopic examination and finally instrumental methods of identification. The combination of two or more of these methods is usually recommended for more accurate results. This review was important at the beginning of this research because it was essential to find the most applicable methods so as to answer the questions and meet the expectations with the most approachable ways.

Solubility

Solubility tests are of great help in a simple chemical laboratory in order to separate fibres in bulk. The chemical structure of polymers in a fibre determines the fibre's basic solubility characteristics, and the effect of solvents on fibres can aid in the general fibre classification. Various classification schemes involving solubility have been developed to separate and identify fibre. The solubility characteristics of every fibre are dependent on the physical structure of the fibre, the molecular weight, crystallinity, chemical composition, orientation and extent of cross-linking and the whole test is based on the tracing of the right solvent to dissolve the right fibre (Timar-Balazsy and Eastop 1998, 385).

Burning tests

The reaction of fibres to heat from an open flame is a useful guide for their identification. The nature of the burning reaction is characteristic of the chemical structure of the fibre. The odour

of gases coming from the decomposing fibres and the nature of any residual ash are characteristic of the fibrous polymer being burned (Timar-Balazsy and Eastop 1998, 381).When thermoplastic fibres are brought close to a flame, they will melt, fuse, and shrink, whereas non thermoplastic fibres will brown, char, or be unaffected by the flame. On contact with an open flame, fibres of organic polymers will ignite and burn. On removal from the flame, fibres will either self extinguish or continue to burn (Needles 1981). Very often this method is used in conservation laboratories for fast identification but it requires a relatively large sample to be destroyed (Timar-Balazsy and Eastop 1998, 385).

To the results for the burning test it must be added that, when appreciable inorganic weighting is present on silk, the latter retains its structure during the burning test, and the inorganic skeleton glows bright in the flame. In such cases, the colour of the ash gives an indication of the nature of the weighting (Koch 1963).

Staining

Staining with suitable mixtures of dyes can identify the different types of fibres. Some fibres have different dyeing characteristics and affinities dependent on the chemical and morphological structure of the fibre. Prepared dye mixtures containing dyes of differing affinities for various fibre types have been used extensively as identification stains for undyed fabrics. Since some fibre types may dye to similar shades with these dye mixtures, two or more stains usually must be used to confirm the fibre content. Staining is effective only for previously undyed fibres or for fibres where the dye is stripped from the fibre prior to staining (Needles 1981).

Microscopic examination

Examination of longitudinal and cross-sectional views of a fibre at some magnifications gives detailed information on the surface morphology of each fibre. As each natural fibre has its

characteristic surface view, positive identification is possible using light microscopy (Needles 1981). Using a simple *optical microscope* one can distinguish some surface characteristics which will help to divide natural fibres into the two major categories (vegetable and animal). Characteristic features on the surface of the fibres can be visible due to the absorption, refraction and reflection of the incident light. For more detailed investigation, *interference microscopy* can be used where light is passing through the sample and gives the opportunity to investigate some inner characteristics of the fibre structure (Timar-Balazsy and Eastop 1998, 382). In *polarized optical microscopy*, the visible light is restricted to a single polarized-plane and structural details of the sample can be detected. It must be noticed however that several chemical processes during finishing or severe degradation can very easily deform the original form and this is an additional complication in fibre identification (The Textile Institute, 1975).

In general, for each of the major class fibres one can easily look for some special characteristics. To distinguish between the different animal fibres one has to observe the pattern formed by the scale margins and its possible variation along the fibre, and the regularity of the fibre thickness. Cultivated silk (*Bombyx mori)* has a smooth surface and cylindrical view. When not *degummed* fibres appear in pairs stuck together with sericin.

Tussah (wild) silk has a flat, ribbon-like appearance with fine longitudinal lines. *Anaphe* silk (another more rare type of wild silk) has perpendicular cross-markings or knobs along their length, looking more like flax filaments and they may be confused with it. Cotton fibres can be easily recognised by the twists formed along the fibre's length. These convolutions are changing directions often, about every 0,4 mm on the same fibre (The Textile Institute 1975).

Fluorescence microscopy gives information contained in an image from a fluorescence microscope that is a combination of chemical and structural features of the specimen. The information collected with this method is based on the fluorescence of some parts of the fibres,

the excitation and emission wavelengths and the intensity of the fluorescence, information which is not normally available under other illumination conditions.

There are two main reasons for applying fluorescence microscopy to fibres, one is to study structurally the fibre itself and second, to locate a substance on the fibre. Many natural and some synthetic fibres have a natural fluorescence at certain excitation wavelengths and this fluorescence is used to investigate the past chemical history of a particular fibre. During processing and finishing, various additives are applied to textile fibres, many of which fluoresce. Most spinning lubricants are oil based and will fluoresce under UV excitation, as well certain antistatic agents and easy-care finishes. Because most domestic washing powders contain optical brighteners, it is possible, using a fluorescence microscope, to tell whether or not a fibre or a fabric has been washed (Greaves and Saville 1995).

Optical and Scanning Electron Microscopy (SEM)

The chief advantage of any type of electron microscopy lies in the increased resolution which it can provide compared to that which can be achieved with light microscopy. The SEM should be compared with the stereo light microscope or the reflected light microscope when its great advantage is the good depth of field. This is complemented by quick and easy specimen preparation in the majority of cases. However, one consequence of the electrons being absorbed into the surface of the specimen is that there is a build up of charge in non-conducting specimens such as textiles. The presence of charge on a specimen may cause the incident beam to be deflected, giving a moving image. The effects of charging can be overcome by coating the specimen with a conducting layer and ensuring that it is electrically continuous with the metallic mounting stub. Strictly, therefore, the image provided is actually that of the conductive coating. The effects of charging on the image can also be reduced by

using backscattered electrons to form the image as these are less affected by charge build up than are the secondary electrons (Greaves and Saville 1995).

Transmission electron microscopy (TEM) is a more specialised method. It measures the net density of electrons passing through thin cross sections of metal-coated fibres and provides a method to look at the micromorphology of the fibre (Needles 1981).

Instrumental methods of identification of fibres

Several instrumental methods can be used for the detailed and positive identification of fibres and their selection is based on the information required and the availability of the equipment.

The qualitative and quantitative analysis of the chemical elements and groups in a fibre may aid in identification and characterisation of a fibre with *elemental and end-group analysis*. Care must be taken in analysis of such data, since the presence of dyes or finishes on the fibres may affect the nature and content of the elements and end-groups found in a given fibre. *Gravimetric* and *instrumental chemical* methods are available for the analysis of specific elements or groups of elements in fibres. Specific chemical analyses of functional groups and end-groups in organic polymers that make up fibres may be carried out (Needles 1981).

In the same way that coloured materials selectively absorb white light, most organic and some inorganic molecules will absorb certain frequencies of IR radiation. The wavelengths which are transmitted or absorbed are determined by the chemical bonds present in the material, and the resulting IR spectrum is characteristic of the compound and may be used for identification. The technique of *Fourier-transform (FTIR) spectroscopy* with the use of a microscope, gives the IR absorption spectrum from extremely small samples, e.g single fibres (Low and Baer 1977). This is obtained because there are some functional groups in the fibre polymer that absorb infrared energy at wavelengths characteristic of the particular group and lead to changes in the vibration modes within the functional group. As a result specific

functional groups can be identified. Functional groups in dyes and finishes also can be detected by this technique (Cardamone 1991, Needles 1981).

The *ultraviolet-visible spectra* of fibres, dyes, and finishes can give information concerning the structure of a fibre, as well as to show the nature of electronic transitions that occur within the material as light is absorbed at various wavelengths. The absorbed energy is either harmlessly dissipated as heat, fluorescence, or phosphorescence or causes chemical reactions, that modify the chemical structure of the fibres. Reflectance spectra are particularly useful in colour measurement and assessment of colour differences in dyed and bleached fibres because colourless impurities do not present interference (Needles 1981, Schweppe 1986, Timar- Balazsky and Eastop 1998).

X-rays diffracted from crystalline or semicrystalline polymeric materials will give patterns related to the crystalline areas within a fibre (Needles 1981, Timar- Balazky and Eastop 1998). This technique is mostly used on archaeological textiles (*see for example*: Kalymaran 1984, Kalymaran 1991), to analyze mineralized fibres (*see for example*: Jakes and Sibley 1985) and for the identification of pigments on textiles (*see for example*: Jaro et al 1987).

Thermal analysis is also used for fibre identification. Specimens are heated at a fixed rate over a given temperature range in a static atmosphere such as nitrogen and physical as well as chemical changes may be investigated. The four most common methods are:

i. *differential thermal analysis (DTA).* The unknown sample is heated together with a known sample, and the differences in absorption or release of energy between the two samples is measured.

ii. *differential scanning calorimetry (DSC).* In this case the difference in energy between the unknown and the known sample is measured. The method proved useful for positive identification between modern and excavated wool (Burges 1990).

iii. *thermal gravimetric analysis (TGA)* The basic fuction of this method is the measuring of the weight change of the fibre sample when the temperature is raised (Accetta and Baumgart 1980).

iv. *thermal mechanical analysis (TMA),* which is used for the investigation of physical properties of deteriorated wool and silk (Burges 1990).

7.3 Fibre identification on historic samples

The first stage of fibre identification on the selected historic samples was performed mainly by microscopic investigations. The small size of the samples and their rareness and importance was the major factor in selecting methods of identification. Investigation under a light microscope is a non-destructive technique that gives satisfying information about the type and the colour of the fibres. After due consideration, solubility tests were also selected, because a single fibre is sufficient to give satisfactory identification, without damaging large quantities of valuable sampling material. The results of these two methods are presented here:

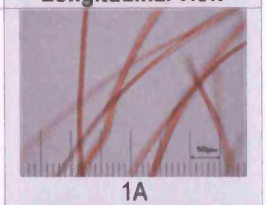
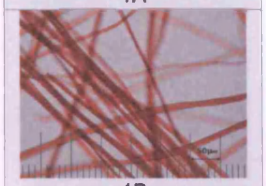
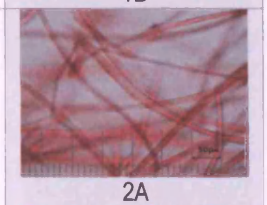
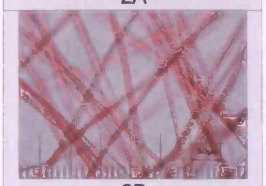
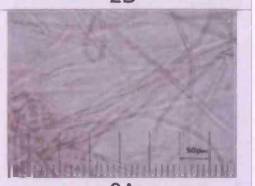
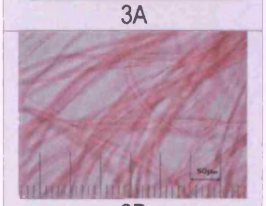
7.3.a Microscopic identification

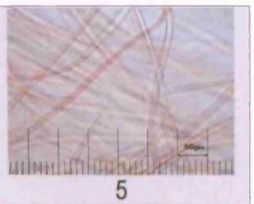
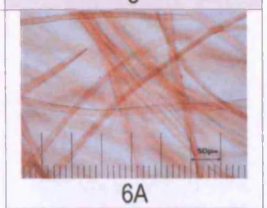
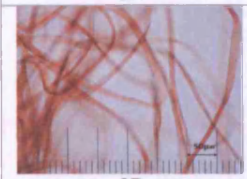
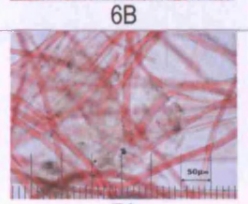
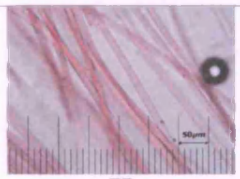
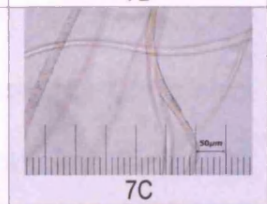
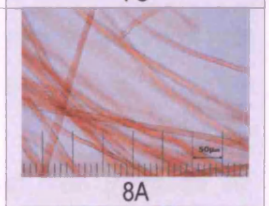
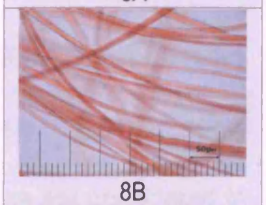
All samples were first studied under a stereomicroscope Olympus SZ-PT, and were easily classified into groups of different types of fibres. Among the samples taken from the Museum of Greek Folk Art in Athens, there were silk, wool and cotton threads. From the two other museums, the Byzantine and Christian Museum of Athens and the Benaki Museum, only silk samples were collected from ecclesiastical textiles and garments. With the macroscopic and microscopic investigation, it was easy to separate them (full photographic documentation of microscopic investigations are given in *Appendix A, section A2).* For this study, only the silk samples were chosen for further examination as already mentioned (see Table 6). Wherever possible, two samples were collected from each garment, from the front and the back. As the front was more exposed to light during display, there are some noticeable differences in colour. All samples were examined in magnifications x2.5 and x5 times. The samples labelled with the

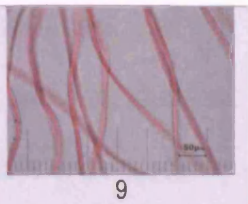
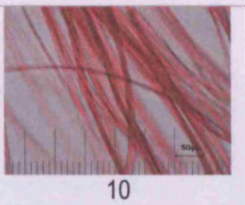
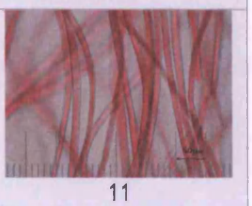
letter A are the ones coming from the front of the garment (more exposed) whereas the others labelled with B are those coming from the back (unexposed). The samples 7a,b and c were taken from the same object (front side) but each one of them has a different colour, therefore they may be dyed with different dyes and it is possible they are made of different kinds of silk although by macroscopic investigations they look the same. The reverse of the garment was not accessible as it was lined with another textile material, so there is no A and B sample taken from this piece. Similarly, there are no A and B samples for objects 5, 9, 10 and 11.

Following this first classification of the available samples, interference optical microscopy was used for more detailed observation of single fibres of the selected silk samples. The samples were prepared for this type of examination on glass slides with the addition of one drop of glycerine/water solution (50:50) and covered with glass cover-slips. This is a temporary method of mounting fibre samples and it was preferred in this case, because the samples were prepared for single fibre identification. Glycerine was preferred as a mounting medium because it has a refractive index of 1.473 which is suitable for general identification purposes applied on animal fibres (Wildman 1954, 23). The preliminary conclusions from the examination of the samples with simple microscopic techniques are summarised below in Table 8. In the table, two representative photographs are given; the first is presents the view of the sample under the stereomicroscope, where the longitudinal view as well as the actual colour of the fibres is detected. In the second photograph, the longitudinal view and some inner characteristics of the fibres are visible under the interference optical microscope.

Table 8. Microscopic investigation of the selected historic samples

Sample	Observations	Longitudinal view
1A & 1B	Silk fibres of fine degummed silk, dyed with a dark red colour in a quite homogenous way. Some areas appear to be lighter in colour as more exposed to light, due to the spinning of the fibres in order to turn them into threads. The most exposed parts of the threads seem to have faded by light. The sample A seems to have no significant differences in colour from sample B.	 1A  1B
2A & 2B	Silk fibres of degummed silk, dyed to a dark red colour. The fibres look thicker than the previous sample. As in sample No1, there are some darker areas along the threads, possibly those that were not directly exposed to light. Some difference in colour, between samples A and B can be observed as sample A appear lighter in colour and has an orange shade.	 2A  2B
3A & 3B	Silk fibres of very fine and curly silk. It looks as if it is degummed silk but the fibres do not look clearly separated. The colour is a light pink not evenly applied as darker and lighter areas can be observed on the same fibre. There is a noticeable difference in the colour of the two samples A and B as the first one looks quite faded in colour.	 3A  3B
4A & 4B	Silk fibres of degummed silk, dyed with a dark red colour. As samples No1 and No2, there are noticeable differences in colour along the threads, as the protected from light areas are much darker. There is no significant difference in the colour of the two samples A and B.	 4A  4B

5	Silk fibres of fine degummed silk, dyed in orange red colour. Again, some areas appear to be lighter in colour along the fibres due to uneven dyeing and partial exposure to light.	 5
6A & 6B	Silk fibres of degummed silk, dyed in dark orange red colour. The dyeing seems quite homogenous although darker areas can be seen due to the spinning of the thread. There are no interesting differences in colour between the samples A and B.	 6A  6B
7a	Silk fibres of fine degummed silk, dyed in dark red colour.	 7A
7b	Silk fibres of fine degummed silk, dyed in orange red colour.	 7B
7c	Silk fibres of fine degummed silk, dyed in yellow green colour	 7C
8A & 8B	Silk fibres of degummed silk, dyed in orange red colour. The colour looks very homogenous and bright and there is no noticeable difference in colour between the back and the front of the garment (samples A and B).	 8A  8B

9	Silk fibres dyed with dark red colour. There are no A and B samples in this case as the sample is taken only from the front side of the garment. The back was lined with another fabric and therefore was not visible. In this case, the sample is taken from a plain fabric and not from embroidery threads and it was cut from frayed areas at the edges of the textile piece. The fibres look uniformly dyed and have the typical appearance of cultivated silk.	 9
10	Silk fibres of dark red colour can be observed on the face of the fabric, called *Byzantine red* by archaeologists and historians (Hatzidaki 1953, Benaki records, 1998). In this case, a small piece of fabric was collected where the weft and warp structures of the fabric are clearly visible. It has to be mentioned here, that the warp yarns are a different colour from the weft, whereas the first are pale yellowish (maybe not even dyed at all, retaining the natural colour of the silk fibres) and the second are dyed to a dark red colour which is mostly visible. From the appearance of the fabric, it is assumed that it has a filling-faced structure (Hatch 1993).	 10
11	Silk fibres dyed in dark red colour. This sample has the same structure as the previous one No10 as they are both taken from similar objects.	 11

7.3.b Solubility tests

Protein fibres can be identified by solubility tests if they can be dissolved in different solvents. For silk fibres, the two main categories are *Bombyx mori* or cultivated silk (degummed or not) and wild *Tussah* silk. The two types can be easily distinguished, as they are soluble in different reagents. The first one (*Bombyx mori*) is readily dissolved in calcium chloride in formic acid, whereas *Tussah* silk is only dissolved in concentrated sulphuric acid. All types of wool and hair fibres are insoluble both these reagents.

In order to perform the above solubility tests, the first solution was prepared by dissolving 10g of anhydrous calcium chloride in 100ml of 90% aqueous formic acid. The fibres were immersed in the solution, using a fresh portion of the fibre each time, at room temperature, using a fibre to liquor ratio of approximately 1:500. The fibres are considered to be insoluble if they remain undissolved after 15min. The results of these tests can be seen in the following Table 9.

For sample No1 to No6 and No8 , there is no need to test both SampleA and B as they are taken from the same thread, where samples No7a, 7b and 7c are from the same object but different threads and therefore there was the possibility they are different types of silk fibres.

Table 9. Results of solubility test on historic samples

Sample	Reagent	Solubility	Time	Results
1	calcium chloride/ formic acid	soluble	3min	*Bombyx mori* silk
2	calcium chloride/ formic acid	soluble	2min	*Bombyx mori* silk
3	calcium chloride/ formic acid	soluble	2min	*Bombyx mori* silk
4	calcium chloride/ formic acid	soluble	5min	*Bombyx mori* silk
5	calcium chloride/ formic acid	soluble	5min	*Bombyx mori* silk
6	calcium chloride/ formic acid	soluble	3min	*Bombyx mori* silk
7a	calcium chloride/ formic acid	soluble	2min	*Bombyx mori* silk
7b	calcium chloride/ formic acid	soluble	5min	*Bombyx mori* silk
7c	calcium chloride/ formic acid	soluble	5min	*Bombyx mori* silk
8	calcium chloride/ formic acid	soluble	2min	*Bombyx mori* silk
9	calcium chloride/ formic acid	soluble	2min	*Bombyx mori* silk
10	calcium chloride/ formic acid	soluble	5min	*Bombyx mori* silk
11	calcium chloride/ formic acid	soluble	4min	*Bombyx mori* silk

7.4 SEM microscopy- fibre identification on historic samples

A Scanning Electron Microscope (S.E.M) Hitachi, S-570, was used for the final investigation of the samples in order to identify the fibres used. For the specimen preparation there are two aspects to providing a pathway for electrons to earth: the first is bonding the sample to the metallic stub; then coating the whole assembly with a thin conductive layer.

Traditionally, the specimen has been bonded to the stub using a conductive adhesive such as colloidal graphite. The drawback to this method is the time which is required for the solvent to evaporate from the adhesive. Also in this case the natural fibres would absorb the liquid adhesive. In practice, the use of double-sided adhesive tape or adhesive tabs, which can be coated instantly, appears to work satisfactorily (Greaves and Saville 1995). The preparation of the samples was made by cutting away a small quantity of fibres and placing them with a pair

of tweezers on a metallic stub under a stereomicroscope, as it was quite a delicate procedure. The fibres were bonded to the specimen stub with the use of a conductive double-sided adhesive tape so as their longitudinal view was visible.

The main requirement for the coating material is that it should have a high electrical conductivity together with a grain size which is sufficiently fine that it does not limit the resolution which is required from the specimen. The coating also affects the electron scattering properties of the specimen (Greaves and Saville 1995). All samples were covered with gold with the metal evaporation method. In this method, the metal to be evaporated is heated in a high vacuum environment by passing a high current through a wire basket or boat containing the metal. The metal evaporates off in the high vacuum in the form of a spray that travels in all directions from the source (Greaves and Saville 1995).

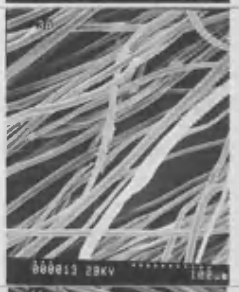
Gold covering was chosen, after testing with other samples of textile materials, because it offers a better and clearer image of the sample. Carbon coated samples showed a heavy charge in the image and it was impossible to investigate the surface of the fibres, although it permits the X-ray analysis of the samples. During the investigation of the samples in the SEM, it was possible to study their surface at very high magnifications such as 2000 times. Looking at their structure it is therefore possible to identify not only the type of fibres but also the exact species the fibres come from. For example, in the case of silk fibres, the commonly used *Bombyx mori* silk filaments are fine, uniform and without internal visible structure. *Tussah* silk filaments are coarser and in longitudinal view they are ribbon-like showing a striated and granular structure, whereas *Anaphe* silk fibres are characterised by transverse lines across them at frequent intervals"(The Textile Institute 1985,12,13).

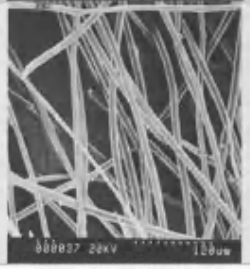
Finally it was possible to establish the thickness of the fibres by measuring the diameter of a fibre at high magnification. Every sample was investigated at two major

magnifications: at x500 times so as to have general views of the fibres and at x2000 where there was a very close view of one single fibre.

The application of SEM to textiles is mainly confined to the study of their surface topography, because the technique is not suitable for studying the internal structures of fibres. The general observations for every sample are listed below in Table 10:

Table 10.SEM investigation of historic samples

Sample	Observations	View
1A & 1B	Uniform fibres with clear cylindrical shape, characteristic appearance of *Bombyx mori* silk. In higher magnifications round dark stains in the surface of the fibres can be observed. The diameter of the fibres measured about 8μm, which is considered a medium to fine fibre. The fibres are well separated with no trace of sericin on their surface, therefore it is a clearly degummed silk.	
2A & 2B	Cylinder unvaried fibres of *Bombyx mori* silk, well separated indicating that the sericin has been removed (degummed silk). The fibre diameter varies from 9μm to 12μm, which can be considered a medium to thick silk. Their surface is quite clear and their shape is regular and familiar.	
3A & 3B	*Bombyx mori* silk fibres but not so uniform and clear. In the magnification x500 they look quite curly. Although that they are separated with one another, their surface looks rough and full of convolutions. This means that they are not completely free of sericin as some of them appear like twin continuous filaments twisted together. Their diameter in the high magnifications, was found to be 6-9μm which is a fine silk	
4A & 4B	*Bombyx mori* silk fibres, very uniform and clear. They are definitely degummed silk fibres and their diameter can be measured at high magnifications, to be 12μm, which places them in the category of medium to thick fibres.	

5	*Bombyx mori* fine silk fibres. The surface is not very clean and uniform, there are convolutions and irregularities along their surface which is probably due to the presence of traces of sericin on their surface. The diameter of an average fibre is 6μm, which is a quite thin silk fibre.	
6A & 6B	Silk fibres with a quite damaged and irregular surface. From the cylindrical shape it is assumed that this is also a *Bombyx mori* degummed silk with an average fibre diameter of 7-8μm .This indicates a medium size silk fibre but among them there are some exceptional bigger fibres of 21μm or more, which indicates the presence of either another type of silk fibre or a general irregularity of the fibres due to the exact species they come from. In some cases, on the surface small attached particles can be observed, possibly of sericin or any finishes not properly removed.	
7a	Silk *Bombyx mori* fibres that show a very irregular surface. The surface of the fibres appears to be abraded and full of flakes. This may be due to its age, as it is one of the oldest samples, and its use. On the other hand, this view of the surface can be ascribed to non-satisfactory removing of the sericin from the fibres, as it looks as if there are some materials on the exterior of the fibres. It may be also, due to the presence of impurities or corrosion products from the two metals (gold and silver) that these fibres were associated with. The diameter of the average fibre can be measured to be 12μm.	
7b	This is also a *Bombyx mori* silk sample as the fibres are fine and uniform. In this case too, it is a comparatively old sample and, the surface shows significant fatigue. The diameter of the fibres is medium in size, and can be estimated to be 1μm.	
7c	Fine and uniform fibres of cultivated silk (*Bombyx mori*). These fibres also appear to have an abraded surface coming from the same garment as the previous two specimens. As mentioned above, this may be due to the presence of sericin, other impurities or corrosion products. The diameter of the typical fibre is 9μm.	
8A & 8B	Degummed silk filaments, fine and uniform, indicating *Bombyx mori* cultivated silk fibres. The fibres have a very clean and smooth surface which vary in diameter along the same fibre, from 6μm to 12μm.	

9	*Bombyx mori* silk fibres sometimes twisted along their length. The surface, although it appears smooth, shows areas with flakes and convolutions indicating some degradation of the fibres	
10	Thin silk fibres with the characteristic appearance of cultivated silk. The surface of the fibres looks eroded in some areas. In some cases the fibres are entirely curly, possibly caused by extensive mechanical stress or chemical damage. The average diameter of the fibres can be estimated at 10μm	
11	Uniform silk fibres, belonging to the category of cultivated *Bombyx mori* silk, with no trace of sericin on their surface. In areas, small particles can be observed along the surface that may be either impurities or degradation products. The average fibre appear thicker this time, with a diameter of 15μm.	

Table 11. Results of fibre identification of historic samples

Sample	Longitudinal View	Type of fibres	Average fibre diameter	Solubility in calcium chloride/ formic acid	Condition
1	Fine, uniform fibres with clear cylinder shape	Bobmyx mori, cultivated silk	8µm	soluble	well preserved
2	Medium to thick fibres, smooth nearly structurless	Bobmyx mori, cultivated silk	9-12µm	soluble	well preserved
3	Not so uniform and clear fibres, but cylindrical	Bobmyx mori, cultivated silk	6-9µm	soluble	degraded
4	Medium to thick, fine fibres with smooth surface	Bobmyx mori, cultivated silk	12µm	soluble	well preserved
5	Fine fibres with not very uniform surface	Bobmyx mori, cultivated silk	12µm	soluble	degraded
6	Cylindrical medium fibres with irregular damaged surface	Bobmyx mori, cultivated silk	7-8µm	soluble	degraded
7a	Medium diameter fibres with damaged surface	Bobmyx mori, cultivated silk	12µm	soluble	highly degraded
7b	Fine uniform fibres but with irregular surface	Bobmyx mori, cultivated silk	10µm	soluble	highly degraded
7c	Uniform cylindrical fibres, abraded irregular surface	Bobmyx mori, cultivated silk	9µm	soluble	degraded
8	Clean , smooth surfaced fibres with variable diameter	Bobmyx mori, cultivated silk	6-12µm	soluble	well preserved
9	Cylindrical smooth, sometimes with flakes surface	Bobmyx mori, cultivated silk	6-8µm	soluble	well preserved
10	Cylindrical fibres, degraded surface sometimes twisted	Bobmyx mori, cultivated silk	10µm	soluble	degraded
11	Thick uniform fibres, surface full of impurities	Bobmyx mori, cultivated silk	15µm	soluble	well preserved

7.5 Mordant identification methods

Two basic identification techniques have been used by researchers for the identification of mordants usually used prior to dyeing on historic and archaeological textiles, X-ray fluorescence and scanning electron microscopy with energy dispersive X-ray analysis (Timar-Balaszy and Eastop 1998).

X-ray fluorescence was the first method to be used by researchers (*see for example:* Darlymple 1983, Darlymple 1984, Green and Daniels 1990, Masschelein-Kleiner and Maes 1978) and it is considered a non destructive technique as there is no need for a sample to be taken from the object. The object to be analyzed is irradiated with X-rays. After irradiation the elements of the irradiated material fluoresce and re-irradiate X-rays of lower energy. The intensity of the reflected energy is measured by a detector which gives a spectrum of peaks. In this way bulk qualitative and quantitative analysis can be done on the given sample. This technique it is considered to be more sensitive to higher atomic number elements like chlorine and sulphur (Green and Daniels 1990, 10). Some of the mordants known to be used in historic textiles are aluminum, copper, iron and tin until the discovery of chromium mordant in the late 19th century, which replaced all the others, because of its better performance and ease of application (Ponting 1980). Although X-ray fluorescence technique can be used directly on the object, if not applied in a vacuum chamber, lower energy X-rays coming from lower atomic number elements will not be detected (Green and Daniels 1990, 10). However, not every textile object can fit into the vacuum chamber and, even if it does, this is not always safe for the object. Also, even with the use of a vacuum chamber, XRF is not as sensitive to lower energies as SEM(EDAX) (Green and Daniels 1990).

The identification of the mordants used on the samples was performed by *scanning electron microscopy with energy dispersive X-ray analysis.* This technique was selected because it can be used to analyse elements as low as sodium in atomic number and it would

be able to identify mordant elements such as aluminium, tin, copper and iron (Jakes and Angel 1985).

The method works by irradiation of the sample with an electron beam, resulting in the emission of characteristic X-rays, which are recognised by a detector. This technique is regularly acknowledged as non-destructive. However, in the case of textile fibres, which are non-conductive materials, there will be a charging, meaning that the electrons will not be conducted away from the surface of the sample. Therefore it is essential to specially prepare the samples by covering the fibres with carbon, before the analysis (Green and Daniels 1990).

The age and the nature of all the selected samples give a prior indication of the mordants used. The objects, where the samples are taken, are historic textiles of 16th to the beginning of 19th century. The samples are all natural silks, dyed with natural dyes of reddish colour. For this kind of material the probable mordant used is alum (aluminium sulfate), as at that time, this was the only mordant used for making red hues on silk (Legget 1944, Hofenk de Graaff 1969, Ponting 1980, Needles 1981, Liles 1993, Dean 1998). The only exception could be the safflower dye which was generally used without pre-mordanting the silk fabric, in order to give a salmon pink colour (Ponting 1980, Liles 1993, Dean 1998).

7.5.a Sample preparation and analytical technique

The samples were prepared by cutting away single fibres and gluing them flat on a metallic stub with the use of a conductive double-sided adhesive sticker. In this way the surface of the fibres was visible and perpendicular to the direction of the incident radiation (Green and Daniels 1990). The samples were covered with a thin film of carbon, by the carbon evaporation technique in a vacuum. This type of coating is usually used for specimens which are to be X-ray analyzed but which need a conductive coating, as carbon does not interfere as much with X-ray analysis as a metal coating would do (Greaves and Saville, 1995).The samples prepared before, for the identification of the fibres, were not suitable for the EDX analysis because they

were covered with gold. The gold covering will not allow the electrons to penetrate the surface of the fibres and therefore the main element to be detected will be gold.

Analysis was performed on each sample, using an accelerating voltage of 20kV and a counting period of 100seconds. In all samples, aluminium was detected, except in the pale-pink one, possibly dyed with safflower which needs no mordant. Some traces of other elements can be explained by contamination of the samples by external factors such as pollutants, water, detergents or contact with other materials. For example calcium and silicon detected in some of the samples, are probably contaminants from water during dyeing or washing. It is also possible for some weighting materials to be detected with this method, such as inorganic salts of iron, lead, tin or zinc (Bogle 1979, Miller and Reagan 1989).

The SEM (EDX) analysis proved useful for the qualitative analysis of the dyed samples, but unfortunately it is not reliable for quantitative analysis of the elements detected (Koestler 1985, Green and Daniels 1990). Because the spot analysis performed by SEM (EDX) is sometimes affected by the lack of homogeneity along the fibres, three analyses were undertaken for each sample. More detailed results of the analyses are summarised in the following Table 12.

Table 12_Mordant identification on historic samples

Sample	Elements Detected			Counting	Mordant
	Analysis 1	*Analysis 2*	*Analysis 3*	*Period / sec*	
1	S, Ca, Al	Al, Si, Ca, Cu, Mg	Si, Ca, Fe, Al	109s	Alum
2	Al, P, S, Ca, Cu	Si, P, Ca, Fe, Al	P, S, Ca, Al	109s	Alum
3	Al, S	S, Al, Zn	Al, S	109s	Alum
4	Si, P, S, Ca, Fe, Al	S, Ca,Cu,Al	Mg, Al, Si, P, S, Fe, Cu	110s	Alum
5	Si,S, Ca, Zn	Si, S, Ca, Zn	Si, S, Ca	109s	none
6	Si, S, Ca, Al	Si, S, Mg, Al	S, Zn, Ca, Al	111s	Alum
7a	Si, S, Fe, Al,	Al, Ca, Fe, Cu	Si, S, Ca, Fe, Al, Cu	111s	Alum
7b	Al, S, Ca, Fe, Cu	Al, Ca, Fe, Pd	S, Ca, Al, Fe, Cu	118s	Alum
7c	Si, P, S, Ca, Al	Si, S, Ca, Fe, Al	Si, P, Ca, Fe, Al	111s	Alum
8	Al, Si, S, Cu	Al, Si, S, Ca	Al, S, Ca, Cu	109s	Alum
9	Si, S, Ca, Fe, Cu, Al	Al, S, Ca, Fe	Al, Si, Ca, Fe, Cu	110s	Alum
10	S, Ca, Al	Al, S, Ca, Fe	Al, S, Ca	110s	Alum
11	P,S, Ca, Cu, Al, Zn	Si, Ca, Cu, Zn, Al	Si, S, Ca, Cu, Al	110s	Alum

7.6 Dye identification methods

The identification of the dyes on the original historic samples proved to be the most complicated of all the identification methods. This is because dye identification methods demand quite a large quantity of sampling material (usually 2g of dyed fibres or textile) and all of them are destructive analytical techniques. Solubility, staining tests and TLC (Thin Layer Chromatography) are methods mostly used for dye identification and they are relatively simple to perform in a chemical laboratory, giving useful information about the type of dyes used on historic and archaeological textiles.

The red natural dyes firstly expected to be found in these samples were the commonly known : madder (*Rubia Tinctorum*), kermes (*Coccus Illicus*), cochineal (*Dactylopius coccus)* and lac dye. The less important: were annatto (*Bixa Orellana),* alkanet *(Alkana tinctoria),* brazilwood *(Caesalpinia eshinata)* and safflower (*Carthamus tinctorius*) (Ponting1980). From

these, the most expected ones are madder, safflower and kermes because they are known as textile dyes even from the ancient Greeks and they were regularly used in the Mediterranean until the introduction of synthetic dyes. Other possibilities include brasilwood, which was introduced to Europe in the 15th century, and annatto, which came from the near East, where the Greeks had trading connections. Also cochineal was a commonly used natural dye after 1525AD, when Spaniards first brought it to Europe from Mexico. Finally, lac dye came to the Mediterranean from Indo-China, Siam and Southern India from sailors traveling regularly to these countries (Legget 1944).

The first question regarding the dyes used in the given samples is whether they are natural or synthetic. As there was no scientific evidence that there are only natural dyes used on these embroideries, it was necessary to make some preliminary tests.

Generally, the identification of dyes on natural textile materials is best achieved with chromatographic and spectroscopic methods. However, when the textile materials are quite old and the dyes are of poor light fastness, the proportion of undestroyed dye is small. A comprehensive review of the identification methods usually used for archaeological and historic textiles lead to the choice of an appropriate procedure.

Solubility and chemical treatments

To identify the dye used in a historic textile material, the first thing is to use some simple preliminary tests so as to put it into the correct group of natural or synthetic dyes. This can be achieved by the solvent stripping test, when the bleeding of the dye can be investigated by immersing a small sample in a solvent. The solvents used in this test are usually water, ethanol, glacial acetic acid and ammonia used in this order. The extent of bleeding of the dye in each solvent gives an indication of the presence of certain dye classes. Synthetic dyes bleed easily in boiling solvents, whereas most of the natural dyes bleed very lightly or not at all.

There are two simple chemical reactions that can be used in order to determine the presence of synthetic dyes. First, zinc dust can be added to the ammonia in which a dye has bled heavily. If the solution becomes irreversibly colourless, this is an indication of the presence of acid or direct dyes. The second test is based on the colour produced from sulfuric acid when it is dripped onto a small sample of the dye. When colours like magenta red, red-violet, violet, blue and green are observed in the solution, it is an indication of synthetic dyes.

On the other hand, when dyes have shown little bleeding in the solvents mentioned above, there are some other simple chemical tests to determine if they are natural dyes. This can be done by boiling a sample of dye for a short time in 10% sulfuric acid. If the solution becomes almost colourless, it is an indication of dyes in the class of hydroxyflavones. Iron tenant dyes have the same reaction where iron can be detected in the solution. A bleeding of a red shade shows the presence of brazilwood and logwood whereas orange bleeding is an indication of madder mordanted on alum or iron sulfate. The same reaction can be detected with insect dyes, like cochineal, kermes and lac dye.

For the natural mordant dyes, it is known that there are a variety of different shades depending on the mordant used before dyeing (*see also 1.3.c).* Having in mind that in the past, a second mordant was added in an already mordant dyed textile, in order to obtain a different shade, natural mordant dyes can be identified using this method. This is done by boiling the samples in dilute solutions of different mordants, such as tin chloride, aluminium sulfate, iron sulfate, copper sulfate, and uranyl acetate. The shades produced depend not only on the salts used but also on the existing mordant dye.

The problem that quickly arose with the collected historic samples is that the sampling material is very restricted and it is not possible to use a large quantity of it in order to perform all the above mentioned tests and then forward them to analytical techniques for the identification of the dyes.

The need to have quantitative as well as qualitative results, in order to match the original dyestuffs and dye combinations when preparing the new samples, as well as the restricted sampling material (some single small threads or fibres weighing less than 1g) meant that the above mentioned methods could not be used. It was obvious that the small size of the samples was leading to the application of more sophisticated instrumental methods of examination of dyes.

Instrumental Methods of Identification of Dyes

The first instrumental method to be used for dye analysis was *UV/visible spectroscopy* (Daniels 1983, Dalrymple 1983). Other methods of spectroscopy were tested over the years with relatively satisfactory results (Taylor 1983, Saltzman 1992) , including *Raman microspectrometry* and *diffuse reflectance absorption spectrometry* (Guineau 1989, Guineau 1991) and *three-dimensional fluorescence spectrometry* (Shimoyama and Noda 1993) as non destructive methods used in situ.

Fourier transform infrared microscopy is also used in dye identification (Gillard *et al* 1992) and it is considered a non destructive technique. On the other hand, in the case of coloured textile fibres FTIR is not recommended as the fibres and the dyes of the samples are already deteriorated and the spectra usually show mainly the deteriorated fibre rather than the dye. Also, it does not seem to be a completely non-destructive technique, as the fibres should be flattened, and therefore effectively destroyed, in order to perform an FTIR analysis.

The most successful methods for dye analysis seem to be the chromatographic techniques of which *thin layer chromatography (*TLC) is the most widely used due to its ease of application in a chemical laboratory. Many researchers have used TLC for dye analysis (*see for example*: Hofenk-de Graaf and Roelofs 1978, Schweppe 1988, Schweppe 1989, Taylor 1990, Taylor 1991, Walton and Taylor 1991) as well as conservation laboratories with properly equipped chemical labs (Easthaugh 1985). Sometimes spectroscopic methods and TLC are combined for more positive identification (Daniels 1985).

Recent advances in chromatographic techniques have shown the predominance of *high performance liquid chromatography* (HPLC) for the identification of dyestuffs and the method is tested and used by many scientists (*see for example*: Cardon *et al* 1989, Evans and Truslove 1993, Koren 1994, Massdhelein-Kleiner *et* al 1981, Quye and Wooters 1991, Wooters 1991, Wooters and Verhecken 1987, Wooters and Verhecken 1989, Wooters 1985). This technique appears to be the most successful for the identification of dyes on historic and archaeological textiles, as it combines speed with high resolution and reproducibility and it does not need a large quantity of sampling material. It has the advantage of quantitative analysis and it is possible to use it with the combination of other analytical techniques such as UV-visible spectroscopy or mass spectrometry for peak identification (Wouters 1985).

HPLC is a technique that comes from the application to liquid chromatography (LC) of theories and instrumentation of gas chromatography (GC). An absorbent is packed into a column and the sample is eluted with an appropriate solvent. If a component of the sample is absorbed onto the surface of the solid stationary phase, it will travel down the column less rapidly than another that is weakly absorbed. In this way, it is possible to have a separation of the components if they appear to have different absorption by the solid phase. It is possible to have a liquid stationary phase in the column, where the separation is due to variances in the distribution coefficients of solutes between the stationary and the mobile liquid phase (LLC). After passing through the column, the separated components of the mixture are sensed by a detector over a specified wavelength range, which for the dyes is normally between 200 and 800 nm (Quye and Wouters 1991,48). The output of the detector is an electrical signal, the modification of which is displayed on a potentiometric recorder, a computing integrator or a VDU screen. Most of the detectors in HPLC are selective devices. This means that they do not detect all the solutes that are present in a mixture. So in some of the cases, the solutes that

cannot be detected need to be transformed into a detectable form after they come out from the column (Lindsay 1987,4).

The advantages of HPLC over other forms of chromatography are many and they are generalized in the fact that the column can be used several times without reformation, the resolution achieved is much higher than any other method, and the analysis times are shorter (Hamilton and Sewell 1977,2).

Once the separation is developed, the given chromatogram can give a variety of information concerning the sample. At the beginning, by counting the peaks, one can determine how many are the components of the mixture. Then, with the use of some known standards, it is possible to find the identity and the concentration of each of the compounds. Finally, if the mixture is completely unknown, the peaks can be collected and used in combination with other instrumental methods for their identification (e.g infrared, nuclear magnetic resonance and mass spectroscopy) (Bidlingmeyer 1993).

As mentioned above the natural dyes expected to be found in the given samples are mostly the well known red natural dyes, madder, kermes and cochineal. It is obvious that the variation in species, the extraction and the dyeing techniques, as well as the atmospheric conditions in which the fibres are preserved will have cause more variation in their composition than all the synthetic dyes that have a controlled composition (Wouters 1985, 119). Dye analysis necessarily involves extracting the dye from a small sample, usually a single thread or fibre, taken from an historic textile fragment. This results in an extracted dye that could weigh only a few nanograms, an amount which demands the use of a highly sensitive analytical technique (Koren 1994, 274). All the expected dyes belong to the class of anthraquinones, the basic skeleton of which is 9,10-anthracenedione (Wouters 1985, 119). The hydroxy- and the carboxyhydroxy-anthraquinonoid dyes may be extracted from plants such as the *Rubia tinctorum* (madder) which consist of alizarin and purpurin amongst others. The scale insects

(*Coccoidea*) are another source of carboxyhydroxy-anthraquinonoid colourants and they include kermesic and flavokermesic acids from *Kermes vermilio*, carminic acid from *Cochineal* and laccaic acids A and B from *Kerria lacca* (lac dye) (*see also section 1.3.c)* (Koren 1994,275).

High performance liquid chromatography has been used for the identification of anthraquinone dyes of old textiles. The identification of the peaks produced can be obtained by standard addition and by stop -flow UV-visible spectroscopy. The composition is calculated by integration and correction for molar extinction coefficients. For successful identification some important factors should be taken into account: the climate and crop quality, extraction and dyeing techniques, environmental effects (ageing) and analytical errors. If these factors can be considered, the analysis results could lead to the identification of the exact plant or animal species that has been used for dyeing (Wouters 1984,127).

Prior to HPLC analysis, an extracted dye solution must be prepared using analytical scale-grade solvents. The dyes can be extracted from a singe thread of 1 cm long, according to the procedure appropriate to each chemical class of dye. For the red dyes coming from plant or animal sources and treated with a mordant, the sample should boil at 100 °C in a solution of equal quantities of 3mol/l hydrochloric acid and methanol. The solution should be evaporated for the acid to be removed and then dissolved again in methanol (≈0,25ml). The standard dyes used as reference should be prepared from commercial natural raw dyestuff that also contain carminic acid, alizarin and purpurin (Koren 1994,275).

High performance liquid chromatography is the most powerful technique, as it can achieve separations and analyses that no other form of chromatography gives. Inevitably, there are so many possible pitfalls. The only way to prevent these is to have experience derived from a great deal of experimental work.

Finally *capillary electrophoresis* (CE) is a new tool for separation science which applies high voltages of up to 30kV across a buffer-filled capillary (Evans and Truslove 1993, 38). It

is not a chromatographic technique, but the different velocities of the particles of each component help to make separation and they can be used for the identification of these components. There are different types of CE including *capillary zone electrophoresis* (CZE). The extracted sample is introduced into the capillary. When high voltage is applied, the components, having different charges, go towards the two poles. In this way, the separation begins like moving boundaries that were formed by the components (Pecsok *et al* 180, 97). In the area of dyestuff analysis, CZE coupled to tandem mass spectrometry is used, as CE offers superior separation efficiency and simpler method development. In addition to that, CE can also be used to determine small ions, including inorganic ions, cations and short-chain carboxylic acids that may be present in the dyes as contaminants or additives (Evans and Truslove 1993, 39).

7.6.a Dye identification on historic samples by HPLC

Having in mind all the above mentioned techniques and their limitations, it was decided that the only method that would give the desirable result on dye identification according to the objectives of this research is high performance liquid chromatography.

As is obvious from the above, the precise identification of dyes on the selected samples collected for the needs of this study was an important but very complicated stage. In order to prepare new sampling material similar to the historic samples in question, it was set as a precondition to know the exact dyestuffs used, and their combinations including the exact proportions of each component. The only identification method giving qualitative as well quantitative analysis on historic dyes is HPLC as explained above. On the other hand, the application of the procedure, from the dye extraction to the use of the chromatographic equipment, as well as the interpretation of the results, needs specific expertise and experience, which were not available in the Institute of Archeology, UCL. Therefore it was decided to address the task to a specialist in the field. Dr Jan Wouters is an internationally known scientist

in the field of historic and archaeological dye analysis and head of the analytical department at the "Royal Institute of Cultural Heritage" in Brussels. He has devoted many years of his career as a researcher in the use of HPLC for natural dye analysis (*see for example*: Dutra *et al* 1997, Ferreira *et al* 1999, Petroviciu *et al* 2002,Wouters 1985, Wouters 1987, Wouters 1989, Wouters 1991, Wouters 1998, Wouters 2000).

To identify the dyes on the original historic textile samples, samples were sent to Brussels, where Dr. Wouters and his team used HPLC for dye identification. The full description of the method can be seen in *Appendix A, section A3.*

7.6.b Results from dye identification

HPLC revealed that in all cases, except one, mixtures of dyes were used in order to obtain the desirable colour or hue. The only exception is the safflower dye, which was found alone, because of the salmon pink colour that it produces when applied to silk without pre-mordanting. All other dyes were applied to pre-mordanted fibres and so is safflower but only when a yellow dyeing is desired (*see section 1.3d).*

Among the dyestuffs found, a synthetic dye was identified and therefore this sample (no.3) was excluded from further analysis and use, as only natural dyeings are of interest in this research. The analytical results are listed in Table 13 for each sample.

Table 13. Results from HPLC dye identification of historic samples

Sample	Object	Date/century	Colour	Dyestuff composition (%)[22]	Remarks
1	Shirt border	18th	Red	0.5law, 0.5orh, +ea, 1ag, +ap, 1mu, 66.5al, 29.5pu, 1ru	There are three different dyes mixed .Basically madder *(Rubia tinctorum)* with a trace of tannin, brazilwood and lowson.
2	Shirt border	18th	Red	6,5dcll, 75.5ca, 1orh, 16ea, 0.5fk, 0.5ka, +em	American cochineal *(Dactylopus coccus)*, a trace of brazilwood and tannin.
3	Bed sheet border	18th	Pink	several components of unknown origin, +lu	There is a trace of luteolin which indicates the presence of a minor amount of weld (*Reseda luteola)*. There is also an indication of indigoid dye, the exact nature of which cannot be determined as yet (indigo or woad for instance). Three components occur with spectral characteristics unknown. Spectral features and discolouration reactions suggest the presence of a synthetic dye.
4	Bed spread	18th-19th	Red	35.5ca, 11.5ea, 1ag, 1mu, 35al, 16pu, +ru	Three different sources have been mixed together: a cochineal red, a madder red and tannin. The synthesis of the cochineal red, shows that it probably a Armenian cochineal *(Porphyrophora hamelii)*. The origin of the tannin cannot be distinguished as ellagic acid is formed in all tannin materials upon ageing.
5	Towel	18th	Orange	13ct0, 30ct1, 29.5ct2, 13ct3, 14.5ap	In this sample the only dye detected is safflower *(Carthamus tinctorius)*. In this particular sample, the red safflower dye was used.
6	Bridal bed sheet	Late 18th	Dark red	1.5orh, 29.5ea, 1ag, 2.5mu, 43al, 22.5ru	Three different dyes have been mixed together: a soluble redwood (from *Caesalpinia* species), a madder red (*Rubia tintcorum)* and a tannin.
7a	Epitafios	1620	Violet red	94ca, 3.5ea, 1.5ka, 1al	An insect red was detected, probably Armenian cochineal (*Porphyphora hamelii)* and a trace of tannin.

[22] See table of abbreviations

Sample	Object	Date/century	Colour	Dyestuff composition (%)	Remarks
7b	Epitafios	1620	Orange	1orh, 1.5ea,1ag, 2mu, 63al, 31.5pu	Mainly madder was detected in this sample (*Rubia tinctorum)*, mixed with traces of tannin and redwood.
7c	Epitafios	1620	Yellow-green	81orh, 19ea	Essentially redwood with a trace of tannin
8	Sperveri	18th	Red	2orh, 0.5ea, 1.5ag. 2mu, 60al, 33.5pu, 0.5ru	Three different dyes have been combined in this sample: a soluble redwood, a madder red and a tannin. This is the same combination as sample No6, but the relative amount of tannin is much higher in the latter
9	Epigonatio	16th	Red	95.5ca, +dcll, 3ea, 0.5fk. 1ka	An insect red, possibly Armenian cochineal and trace of tannin.
10a	Epimanikio	19th	Pink ochre	12ca, 68.5orh, 18ea, 1.5in	As in this sample the warp yarns have different colour from the weft, analysis showed different dyes and dye combinations. The pink ochre warp yarns are dyed with redwood, a small amount of an insect red (species impossible to determine), a small amount of tannin and a trace of a indigoid dye. The dark red weft, is dyed with American cochineal *(Dactylopius coccus)*
10b	Epimanikio	19th	Red	90ca, 9.5ea, 0.5ka	
11	Epimanikio	19th	Red	83ca, 1orh, 15ea, 0.5fk. 0.5ka	Three sources are mixed together, American cochineal,a small amount of tannin and a trace of redwood were detected in this sample.

Table of abbreviations for Table 13

Abbreviation	Componet (common name) - source
ag	Anthragallol – madder red
al	Alizarin – madder red
ap	Apigenin – weld, safflower
ca	Carminic acid – cochineal red
ctx	Unknown – safflower
ea	Ellagic acid – tannin
lu	Luteolin – weld
mu	Munjistin – madder red
orh	Redwood degradation product – redwood
pu	Puprurin - madder red
ru	Rubiadin – madder red
fk	flavokermesic acid
ka	kermesic acid
low	lowson

8. Sample Preparation

The intention of this research was to base the experimental work on original material in order to deal with the complications conservators face with historic silks. After the collection of samples from historic silks of Greek and east Mediterranean origin, and the detailed identification of their construction materials, fibers and natural dyes, it was discovered (perhaps predictably) that hardly any historic textile is dyed with one dyestuff alone, but with different dye combinations, making their light fastness properties much more complex.

Following the examination of the original historic samples, model samples were prepared in order to test the inhibitors' effectiveness. The preparation was based on the selection of a particular category of historic silks, according to the samples taken from Greek museums. This category involves silk textile and silk embroidery threads of cultivated Bombyx mori dyed with certain natural red dyes and dye combinations, pre-mordanted with alum mordant, except safflower. By preparing model sampling material and treating it with the selected commercial inhibitors, it was possible to design an experimental plan of artificial ageing with controlled and measurable conditions in the laboratory.

8.1. Silk fabric and threads

For the preparation of the new samples, natural silk fabric and threads were needed, made of cultivated silk without any dyes or finishes. The natural silk fabric was selected from the collection of Whaleys (Bradford) Ltd, 100% silk for dyeing and printing, Habotai silk medium (S14). The silk threads were supplied from the Handweavers Studio & Gallery Ltd, yarn types: 8/2nm (2,7w.c.) and 5/2nm (2/4.5 w.c.). Both fabric and threads were chosen because they are made of

cultivated Bombyx mori silk without any dyes or finishes. Identification of the fibres of the new materials took place with the same methods as described in *Chapter 7*, to confirm the resemblance to the historic material.

Fibres taken from the new silk fabric and silk threads were readily soluble in a solution of calcium chloride and formic acid, an indication of cultivated Bombyx mori silk. Microscopic investigations by light microscopy, interference microscopy and scanning electron microscopy confirmed the identification.

The newly selected material, fabric and threads were investigated in the SEM in order to assess the resemblance to the historic samples. At magnifications of x500 and x2000 the samples showed fine cylindrical fibres with smooth, almost featureless, clean surfaces. This is the characteristic view of the cultivated, sericin-free, silk. Two characteristic SEM photographs in Figure 14 show the resemblance of the new and historic sampling material.

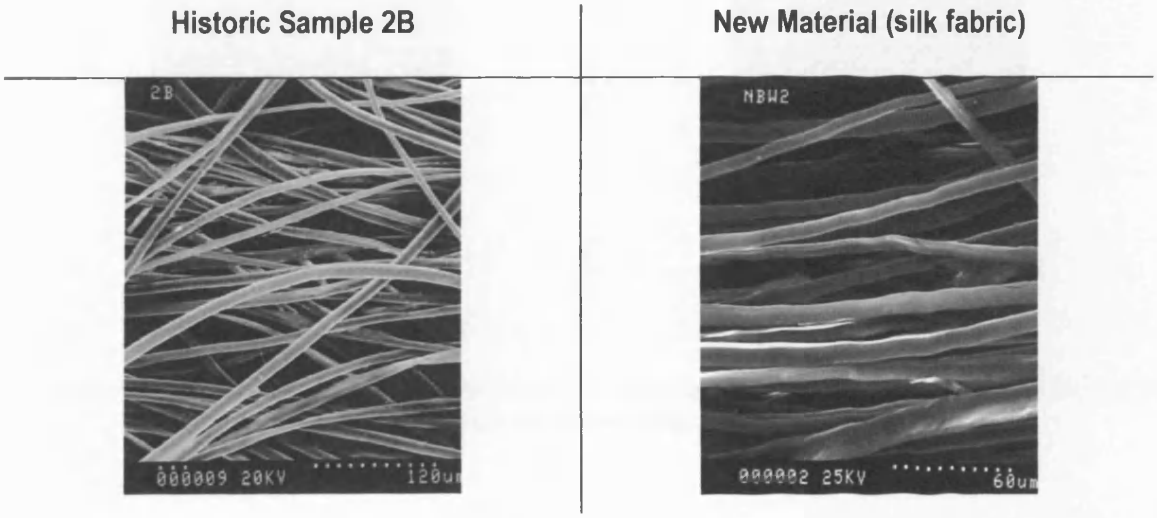


Figure 14. Comparison photographs from the SEM of the historic and the new sampling materials

Although the selection of the new silk fabric and threads was made very carefully and the new materials were chosen to be without any finishes or additives and "ready for natural dyeing" with the confirmation of the manufacturer, one can never assume that they would be exactly the same as a 16th century silk, for example. As silk production is an extremely delicate procedure

and dependent on many factors, several non-avoidable differences would be spotted in the production of the new silk material. First of all, as already mentioned, the quality and form of the silk fibre is mainly dependent on the diet of the silkworm. Silkworms were always fed on mulberry leaves at frequent intervals that must be very fresh, and this was a standard and very important procedure of historic sericulture[23]. Nowadays, silkworms are fed with a mixture of mulberry leaves, cornstarch and soya bean (Bush 2000,12). Also, the historic degumming procedure involved boiling the silk cocoons in water in order to dissolve the water soluble secirin, and separation by hand of the fibres, washing with white soap and then putting on the winding frames. In the modern silk industry, all these procedures are done mechanically and lead unquestionably to cleaner and more uniform fibres.

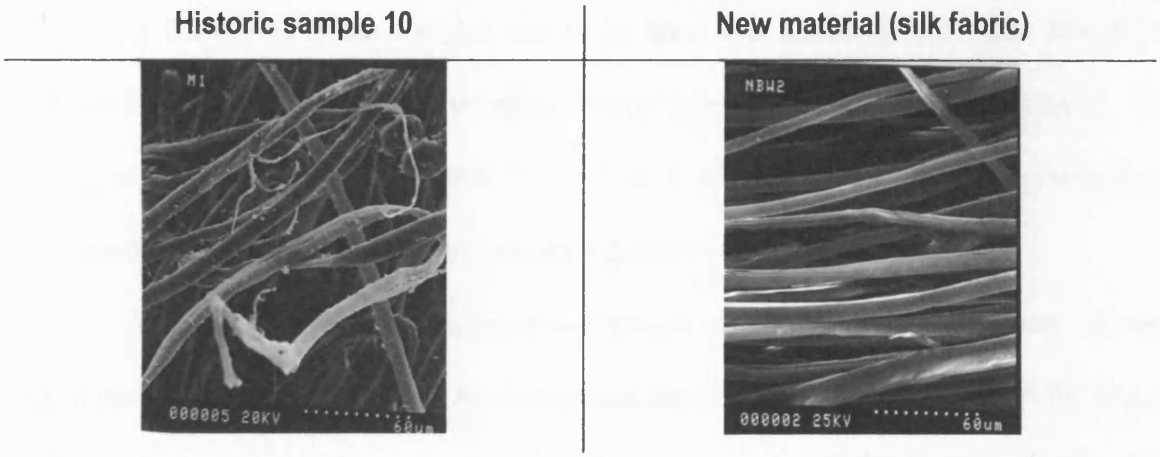


Figure 15. Comparison photographs from the SEM of the historic and the new sampling materials. The fibres on the historic sample are soiled and deteriorated

Finally, the main difference between the new sampling material and the historic samples is the soil depositions, degradation products and general deterioration on the fibre surface of many historic samples in, which is something to expect from textile materials dated from 16th to 19th century. An example of deteriorated fibres coming form the collected historic samples in comparison to the new sampling material is given in Figure 15.

[23] Sericulture: silk production

8.2 Dyeing with natural red dyes and dye combinations

The dyeing of the new material was done with traditional recipes and methods, using the natural sources identified on the historic samples. However, it should be noted that there are many ways of dyeing with the same dyes and very often with the same colour result. Liles (1990) gives, for example, three different traditional recipes for dyeing with cochineal silk fibres. The dyeing methods in historic context vary according to location, available materials and know how and usually were home made procedures. It is therefore impossible to know and to copy the exact procedure used for the dyeing of the selected samples. Nevertheless the basic stages of natural dyeing for silk fibres are more or less the same, such as scouring[24] and mordanting (Fereday 2003) and they were followed in the present research.

As the dyeing of the samples was to be done with traditional techniques in order to achieve similar dyeing conditions, the help of another specialist on the field was requested. The dyeing process took place in the Ashill Colour Studio[25], with the assistance of Mrs. Jenny Dean (specialist in natural dyeing). The same studio supplied the natural dyestuffs.

Pieces of the new materials, fabric and threads, were dyed with all the natural red dyes found on the original samples. The most representative dye combinations, found on the historic samples, were applied to the new materials, to achieve the same synthesis and final colour. The dyes and dye combinations used are:

- Madder red
- Cochineal red
- Safflower pink
- Brazilwood red
- Brazilwood + madder + tannin (as historic samples No6, No7B,No8)
- Brazilwood + madder + tannin + lawson (as historic sample No1)

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[24] scouring : the boiling of the fibres in soap solution in order to clean it thoroughly and remove any gum residues before dyeing.

[25] Ashill Colour Studio, Boundary Cottage, 172 Clifton Rd, Shefford, Beds. SG17 5AH

- Cochineal + brazilwood + tannin (as historic samples No2, No11)

The proportion of each dye in the combinations were achieved in the manner described below and following the dye identification results taken from HPLC analysis of the historic samples.

8.2.a Dyeing with traditional methods

Mordanting

All new material had to be mordanted before dyeing, with alum mordant, except the one piece to be dyed with safflower. The new silk fabric and threads were soaked in warm water with some drops of neutral washing liquid. This is the stage of scouring, where the fibres are cleaned to remove any gum residue that may interfere in the mordanting or dyeing procedures (Fereday 2003). This prepares and helps the fibres to absorb easily the mordant solution. A solution of aluminum sulfate in warm water was prepared using alum equal to 2/3 of the weight of the materials to be dyed. The wetted-out silk was added to the solution when cooled, in a non-reactive vessel. The silk was worked well for several minutes and steeped for several hours. Then, the material was removed, squeezed out and hung up to dry till the next day.

Dyeing with Madder, Cochineal, Brazilwood

The same method was used for dyeing silk with these three dyes. The dye solutions were prepared by boiling the dyestuffs in water for several minutes until the colour of the solutions turned dark red to brown. The dyestuffs used were double the weight of the materials to be dyed each time (in that case 50 g). The quantity of water used to dilute the dyestuff is not important. The dye solutions, after boiling, were well strained to separate the dyestuff pieces (petals, insects, pieces of wood *etc*) and transferred to stainless steel dye pots. More water was added in order to cool the solutions and to produce a volume sufficient to immerse the pre-mordanted fabric and threads. The material was soaked again in warm water with some washing liquid before dyeing and then immersed in the dyebaths for about 1hour for madder, 30min for

cochineal and 45min for brazilwood, keeping the temperature at 50°C.

After removal from the dyebaths, the fabric and threads were well rinsed with clean water and hung up to dry.

Dyeing with Safflower

The safflower petals can give both yellow, when boiled, and a pink colour when used in cold solution on silk. To produce the pink colour, the yellow dye must first be extracted from the petals. The petals were tied securely in a piece of muslin and yellow dye was extracted by squeezing the muslin bag of petals under cold running water until the water ran clear. The petals then were soaked in cold soft water, sufficient for the subsequent dyebath. Potassium carbonate was added to turn the petals red as the dyebath should be alkaline at pH11. After 1 hour in the water the petals were squeezed and strained off.

To the remaining dye liquid, dilute acetic acid was added to bring the solution acidity to pH6. The silk material was immersed to the cold dyebath and left overnight. The next day, silk fabric and threads, having a bright pink colour, were squeezed well and hung up to dry.

Dyeing with dye combinations

The dye combinations were prepared in the same way as the first dyes, by boiling the dyestuffs in water. The dye procedure was exactly the same as above (dyeing with madder, brazilwood and cochineal). This time the dyebaths were prepared by adding different proportions of dyestuffs to the same solution, following the analytical results from the original samples. For combination 1, the synthesis of original sample No6 was used, mixing 97.5% madder, 2% tannin and 0.5% brazilwood. Combination 2 was prepared following the identification results of sample No1, combining 99% madder, 0.5% lowson (coming from henna) and 0.5% brazilwood. Finally, Combination 3, was made in correspondence to sample No11 in order to prepare the Byzantine red hue. For this, 83% cochineal, 1% brazilwood and 15% tannin, were mixed in the dyebath.

8.2.b Identification and evaluation of the new dyed sampling material

Colourimetry

In order to determine how closely the newly dyed samples resembled the historic material, colourimetric measurements were performed on the new samples in addition to those already performed on the original materials. Colour measurement was performed with the use of a Minolta CR-221 chromameter with light source C, a 3mm diameter measuring area, and a 45º illumination angle. These specifications are exactly the same as those used on the original objects. As three measurements were taken each time, the average of the chromaticity coordinates for each sample is given in Table 14, alongside those of the historic objects.

Table 14.Colourimetric measurements of the newly prepared samples in comparison to the historic samples.

Chromaticity coordinates	New samples		Historic samples	
Y	Safflower	34,79	Sample 3	22,62
x		0,3965		0,4191
y		0,3306		0,3232
Y	Comb 1	14,81	Sample 6	7,033
x		0,4806		0,4829
y		0,3461		0,3586
Y	Comb 2	14,33	Sample 1	4,9833
x		0,4694		0,5132
y		0,3476		0,3309
Y	Comb 3	5,95	Sample 11	5,45
x		0,4818		0,4527
y		0,2581		0,299

From the study of the table can be seen that the two chromaticity coordinates, x for hue and y for chroma are very similar in every case showing that, according to the CIE chromaticity diagram (*see section 9.1.a)*, the same colour was achieved in the preparation of the new samples as intended. On the other hand, the coordinate Y for lightness shows great differences; in fact its values are much higher than those of the original samples. This may be due to the age of the

objects the samples are coming from, and the alleged photodegradation these objects may suffer. The only exception seems to be sample 11 (Byzantine red), on which dye combination 3 was based, and which shows only little difference in the coordinate Y. This may be due to two reasons, one is the relatively young age of the object (19th century) and therefore not so deteriorated, and the second is the dye itself. The dye of this sample consists mainly of cochineal (83%), which has a relatively high light fastness.

HPLC dye identification

The investigation of authenticity of the newly prepared sampling material was complemented by HPLC analysis, to confirm the identity of the dyestuffs used.

As with the original material, samples of the newly dyed fabrics and embroidery threads were sent to the "Royal Institute of Cultural Heritage" in Brussels, where they were analyzed by Ina Vanden Berghe, coordinator of the Materials and Techniques Department. The same analytical technique was used, as Mrs Vanden Berghe was informed in detail of the technique formerly used (a copy of the previous report of Dr. Jan Wouters was sent to her). The analytical results are given in Table 14 and a table of abbreviations is also included.

An unexpected observation was that neither brazilwood nor lowson could be identified as components in the dye combinations, while the brazilwood dyed samples were clearly identified in the analysis (sample No2). The analyst attributed this to the very low concentration of the two dyestuffs during the dyeing procedure, in comparison to the other components (madder, cochineal and tannin). There is also the possibility that traces of brazilwood and lowson were washed off after the dyeing procedure[26].

Another observation is the absence of safflower in sample No3. The only components detected on these samples (fabric and threads) were traces of alizarin and purpurin which were attributed to contamination of the column and are not considered part of the analytical result (Vanden Berghe, 2007, 5). This result was really strange since the whole dyeing with safflower

[26] Conclusions derived after personal communication with Ian Vanden Berghe, 2007

procedure and the dye result (salmon pink colour of the fabric and threads) are incontrovertible. The explanation is given again by the specialist involved in the analysis, and is focused on the four unidentified characteristic peaks on which the identification of safflower is usually based. None of these expected peaks were found in the chromatographs and it is pointed out by Vanden Berghe, 2007, that this is a common phenomenon on freshly made samples, as the ones prepared for the needs of this research *(see also Appendix A3.2)*.

Evaluating the authenticity of the newly prepared samples, it is evident from the results of the analytical techniques used, that they resemble the original samples taken from Greek historic objects, but they are not exactly the same. Of course they are all made of cultivated natural silk and they are dyed with natural dyes using traditional techniques. Dye combinations attempted have given interesting colour results rather similar to the original but the HPLC analysis showed no exact resemblance. Some of the expected components are not evident and this is perhaps due to the dye method selected which could not be exactly the same as the ones used on the selected original objects. Finally, the historic samples are already aged and deteriorated and changes have already happened to their chemical structure that cannot be reproduced in the new sampling materials. On the other hand, choosing new silk material and dyeing it with traditional methods, gives us the opportunity to test model samples as similar as possible to the original historic reference material.

Table 15.HPLC analytical results for dye identification on model samples

Sample	Description after dyeing	Composition	Biological sources
Sample 1a	Madder thread	1 ag, 67 al, 1 xp, 30 pu, 1 ru (+ trace ca)	Madder (+trace of cochineal)
Sample 1b	Madder fabric	1 ag, 63 al, 35 pu, 1 ru	Madder
Sample 2a	Brasil wood thread	82 orh+bra (11 al, 7 pu)	Brasil wood
Sample 2b	Brasil wood fabric	91 orh+bra (7 al, 2 pu)	Brasil wood
Sample 3a	Safflower thread	(81 al, 19 pu)	No dyes detected
Sample 3b	Safflower fabric	(83 al, 17 pu)	No dyes detected
Sample 4a	Cochineal thread	ca, ka? No dcII and fk	Cochineal
Sample 4b	Cochineal fabric	+dcII, 100 ca, +ka, +fk !!!!ka before fk !!!! 0,1 dcII, 99.8 ca, 0.1fk ka	Cochineal
Sample 5a	Brasil wood +madder +tannin thread	(+ca), 3 ea, 1 ag, 67 al, 0.5 xp, 28 pu, 1 ru	Madder and tannin (+trace of cochineal)
Sample 5b	Brasil wood +madder +tannin fabric	(1.5 ca), 3 ea, 1 ag, 63 al, +xp, 31 pu	Madder and tannin (+trace of cochineal)
Sample 6a	Brasil wood +madder +tannin +lawson thread	0.5 ea, 0.5 ag, 71 al, 1 xp, 26 pu, 1 ru	Madder and trace of tannin
Sample 6b	Brasil wood +madder +tannin +lawson fabric	1 ea, 1 ag, 64 al, 34 pu	Madder and trace of tannin
Sample 7a	Cochineal+brazilwood+tannin thread	2 dcII, 95.5 ca, 2 ea, 0.5 ka, + fk !!!ka before fk!!! 0.2 dcII, 99.4 ca, 0.4 fk ka	Cochineal and trace of tannin
Sample 7b	Cochineal+brazil+tannin fabric	2.5 dcII, 51.5 ca, 46 ea, +ka, + fk 0.6 dcII, 98.6 ca, 0.9 fk ka	Cochineal and tannin

Table of Abbreviations for Table 15

Abreviation	**Dye Component**
ag	anthragallol
al	alizarin
pu	purpurin
ru	rubiadin
xp	xanthopurpurin
ca	carminic acid
ka	kermesic acid
fk	flavokermesic acid
dcll	fk glucoside
orh	unknown component of soluble red wood
bra	brasilein
ea	ellagic acid
mu	munjistin

8.3. Selection of photodegradation inhibitors

The inhibitors used in this research needed to be selected according to criteria based on the performance, availability, toxicity and conservation restrictions as posed in detail in *Chapter 5*. Many agents have been tested for different purposes but which of them can be used on historic dyed silks as a conservation treatment? The main selection criteria are summarized below:

- Selected photodegradation inhibitors must perform efficiently when applied on polymer materials, plastics, synthetic dyes and natural fibres according to previous research.
- Inhibitors should be commercially available and reasonably priced; in order to be used easily by small museums and collections with restricted funding. Preferably they should be commercial products of well known chemical industries in order to be easily found or imported to different countries.
- The selection should include inhibitors belonging to all the major categories: absorbers, antioxidants and excited state quenchers, with different chemical structures.
- Inhibitor combinations should be tested, in order to investigate if there is a synergetic effect between two main types of inhibitors; the most commonly used, absorbers and antioxidants, which usually synergize between them according to the available literature *(see section 4.2)*.
- They should not be toxic or dangerous in use in conservation laboratories. They must be colourless or nearly colourless, so that they will not affect the colour of the textile material after application.
- They should be soluble in a range of solvents, acceptable in textile conservation, so that they do not affect the fibres or the dyes used.

8.3.a Additives and additive combinations

According to the above criteria and based on the literature, some preliminary information on additives and additive combinations was collected. The basic conclusions of this review are summarized in Table 16. The commercial products presented in this table have already been tested on modern textile fabrics by researchers in industry (*see for example*: Becker et al 1989, Carr et al 1985, Crews 1984, Cristea 2006, Evans and Waters 1981, Rose et al 1961,Thorson 1990, Waters et al 1980).

From the above mentioned additives, with a preference for those reported to perform satisfactorily on natural fibres, a second list was prepared in order to trace these inhibitors in the trade and do some preliminary testing. The selection was made having in mind those which were suggested in the literature as being the most effective on plain silk and wool fibres, and some of them on natural dyes as solutions and on cellulose acetate films. Some of them are widely used today in the textile industry, especially on synthetic fibres and dyes, in order to produce lightfast fabrics. They were also selected by their characteristics (colour, solubility, toxicity) so that they can be acceptable for use on historic textiles as a conservation treatment. Some combinations of these inhibitors were also suggested at the beginning, which seemed to present a synergetic effect and provide better protection. Finally, it was also important to cover as many as possible of the types of additives mentioned in the recent literature. In Table 17 the list of primarily selected inhibitors is given with some chemical and commercial characteristics.

Table 16. Photodegradation inhibitors already tested - collected information from literature

	Inhibitor commercial name(s)	Chemical Class	Remarks
Photodegradation Inhibitors	Cyasorb UV 9	Hydroxybenzophenone	Performed well
	Cyasorb UV24	Hydroxybenzophenone	Did not prevent fading
	Cyasorb UV1084	Butylamine nickel II	Green discolouration
	Cyasorb UV2126	Hydroxybenzophenone	Polymer formulation
	Cyasorb UV 531	Hydroxybenzophenone	Performed well
	Cyasorb UV5411	Benzotriazole	Did not prevent fading
	Cyasorb UV 284	Hydroxybenzophenone	Reduces the phototendering of wool
	Givsorb UV-1	Phenyl formamidine	Oil-based formulation
	Givsorb UV-2	Phenyl formamidine	Did not prevent fading
	Inhibitor RMB	Resorcinol monobenzoate	Insoluble in water
	Inhibitor DOBP	Hydroxybenzophenone	Performed well
	Mark 1535	Proprietary	Caused skin irritations
	Tinuvin P	Benzotriazole	Did not prevent fading
	Tinuvin 326	Benzotriazole	Did not prevent fading
	Ultrafast 830	Hydroxybenzophenone	Dark green discolouration of textiles
	Univul 490	Hydroxybenzophenone	Insoluble in water and tetrachloroethylene
	Univul M-40	Hydroxybenzophenone	Performed well
	Univul MS-40	Hydroxybenzophenone	Performed well
	Univul D-49	Hydroxybenzophenone	Insoluble in water and tetrachloroethylene
	Univul D-50	Hydroxybenzophenone	Insoluble in water and tetrachloroethylene
	Univul DS-49	Hydroxybenzophenone	Only slightly soluble
	Good-rite 3125	hindered phenol	Not significant performance alone on heat and light
	Cyanox 1790	Hindered phenol	Not well performed alone
	Chimassorb 944LD	Polymeric hindered amine	No significant performance alone
	Irganox 1098	Hindered Phenol	No significant performance alone
	Irganox 1425	Hindered Phenol	Synergistic effect with UV absorbers on wool
	Tinuvin 327	benzotriazole	No significant performance alone
	Tinuvin P	Benzotriazole	Reduces the photodendering of wool
	Tinuvin 765	HALS:hindered amine	Quite satisfying performance in prevention of strength loss and very good on colour fading.
	Tinuvin 770	HALS	Quite satisfying performance
Combinations	Tinuvin 327 + Tinuvin 765		Good performance
	Good-rite 3125 + Cyanox STDP(thioester)		Quite good protection
	Cyasorb 531 + Tinuvin 765		Excellent performance 92.1%
	Cyasorb 531 + Tinuvin 770		Very good performance 62.5%

Table 17 .Photodegradation inhibitors selected for preliminary testing

	Inhibitor commerical name(s) and class	Chemical structure	Manufacturer
Photodegradation inhibitors	Cyasorb UV9 (hydroxybenzophenone)	2-hydroxy-4-methoxy-benzophenone	American Cyanamid Co.
	Cyasorb UV531 (hydroxybenzophenone)	2-hydroxy-4-n-octyloxybenzophenone	American Cyanamid Co.
	Inhibitor DOBP (hydroxybenzophenone)	2-4-dodecyloxy-2-hydroxybenzophenone	Eastman Chemical Products Inc
	Univul MS-40 (hydroxybenzophenone)	2-hydroxy-4-methoxy-benzophenone -5-sulfonic acid	BASF Wyandotte Corp.
	Good-rite 3125 (Hindered phenol)	3,5-Di-tert-butyl-4-hydroxydro-cinnamic acid triester with 1,3,5-tris (2-hydroxy-ethyl)-s-triazine-2,4,6 (1H.3H.5H)-trione	B.F.Goodrich Co.
	Tinuvin 327 (benzotriazole)	2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole	Ciba-Geizy Corp.
	Tinuvin 765 (Hindered amine)	Bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate (minor component proprietory)	Ciba-Geizy Corp
	Tinuvin 770 (Hindered amine)	Bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate	Ciba-Geizy Corp.
	No trade name (Hindered piperidine)	2,2,6,6-tetramethyl-piperidine	Sigma Chem. Co.
Combinations	Cyasorb 531 + Tinuvin 765	Benzophenone + hindered amine	
	Cyasorb 531+ Tinuvin 770	Benzophenone+ hindered amine	
	Tinuvin 327 + Tinuvin 765	Benzotriazole+ hindered amine	
	Tinuvin 327+ Tinuvin 770	Benzotriazole+ hindered amine	

8.3.b Pilot tests on selected photodegradation inhibitors

After looking though the British market at the time of this research, and at the available chemical companies, the selection of photodegradation inhibitors was limited to a small number of commercial products. These products went into some pilot tests in order to test their solubility, colour and general laboratory behavior. The tests performed were the following:

- Solubility in water, acetone, ethanol, tetrachloroethylene and white spirit with consideration of the ease and speed of dissolution and the colour of the final solution. These solvents were chosen because of their widespread use in conservation.
- Application of inhibitors to non dyed silk fabric and investigation on the colour changes and possible changes in flexibility, by eye examination

Only 5 inhibitors survived the pilot tests and they come from the two main classes, the absorbers and the antioxidants from which the hindered amines were selected. Combinations of these products were also selected in order to investigate a possible synergetic effect. In Table 18 the inhibitors used in this research are listed, as well as their combinations. Information on the toxicity, physical and chemical properties of the chosen additives is given in Table 18, based on the safety data sheets provided by the chemical companies.

Table 18. Photodegradation inhibitors and combinations used in experimental treatments

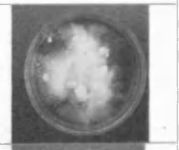
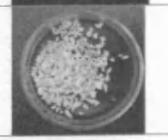
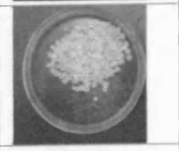
		Commercial names	Chemical structure	Category	Manufacturer	Form	
Photodegradation inhibitors	A	-	2-hydroxy-4-methoxy-benzophenone	absorber	Sigma	Yellow powder	
	B	-	2-hydroxy-4-n-octyloxy benzophenone	absorber	Aldrich	Yellow crystals	
	C	Tinuvin 327	2,3-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl) phenol	absorber	Ciba	Yellowish powder	
	D	Tinuvin 770	Bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate	Hindered amine (antioxidant)	Ciba	White powder	
	E	Chimassorb 944	N,N-bis(2,2,6,6-tetramethyl-4 piperidinyl)-1,6-hexane-diamine polymer with 2,4,6-trichloro-1,3,5-triazine	Polymeric hindered amine (antioxidant)	Ciba	Transparent crystals	
Combinations	F	A + Chimassorb 944	2-hydroxy-4-methoxy-benzophenone + N,N-bis(2,2,6,6-tetramethyl-4 piperidinyl)-1,6-hexane-diamine polymer with 2,4,6-trichloro-1,3,5-triazine	Absorber + Hindered amine			
	G	A+ Tinuvin 770	2-hydroxy-4-methoxy-benzophenone + Bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate	Absorber + hindered amine			
	H	Tinuvin 327 + Chimassorb 944	2,3-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl) phenol + N,N-bis(2,2,6,6-tetramethyl-4 piperidinyl)-1,6-hexane-diamine polymer with 2,4,6-trichloro-1,3,5-triazine	Absorber + hindered amine			
	I	Tinuvin 327+ Tinuvin 770	2,3-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl) phenol + Bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate	Absorber + hindered amine			

Table 19.Hazards identification of the selected photodegradation inhibitors

Photodegradation inhibitors	Commercial names	Hazards	Safety statements
A	- similar to Cyasorb UV9	Irritating to eyes, respiratory system and skin	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing
B	-	Irritating to eyes, respiratory system and skin	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing
C	Tinuvin 327	Harmful: danger of serious damage to health by prolonged exposure if swallowed. Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment	Do not breathe dust. Avoid ignition sources. Avoid contact with skin, eyes and clothing. Prevent contamination of soil, drains and surface waters.
D	Tinuvin 770	Irritant to eyes. Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment	Do not breathe dust. Avoid contact with skin, eyes and clothing. Prevent contamination of soil, drains and surface waters.
E	Chimassorb 944	No special hazards	Do not breathe dust. Avoid contact with skin, eyes and clothing. Prevent contamination of soil, drains and surface waters

8.4 Selection of the solvent

The selection of the solvent for the inhibitor solutions was based on the solubility of the inhibitors in the pilot tests presented above.

To test the solubility, 1% solutions were attempted for each inhibitor. The solutions were prepared in a preconditioned laboratory room, with room temperature at 20°C. Each additive was considered soluble if it dissolved after 10 min of stirring. When an additive was soluble in the solvent, a higher concentration was attempted of 2%, which was the selected concentration for further testing. The results are presented in Table 20.

8.5 Application of photodegradation inhibitors to the samples

8.5.a Application method

The method selected for the application of the inhibitors to the newly prepared samples was the immersion of each sample in the solution. This is an acceptable method in textile conservation as it can be combined with the dry cleaning of textiles with organic solvents. In this way, the textile is not stressed at all and it can be left flat to dry in a few minutes.

The selected concentration for the solutions of inhibitors prepared was 2% and it was based, as a medium value, on the available literature and the successful results reported in it. Researchers have applied inhibitors in concentrations from 0,02% to 5% (Cegarra et al 1972, Water and Evans 1983), while most of them have used between 0,1% to 3% (*see for example*: Cristea 2006, Evans and Waters 1981, Riedel and Hocker 1996, Leaver 1982) or between 2% to 3% for inhibitor combinations (Thorson 1990). The 2% concentration for the solutions was also selected after testing higher concentrations in preliminary evaluation tests that proved to make the fabrics a lot stiffer. For these preliminary tests, non dyed samples of silk fabric were treated with inhibitor and inhibitor combination solutions (where possible) in acetone, ethanol, tetrachloroethylene and white spirit solvent.

Table 20. Results of the pilot tests in solubility of photodegradation inhibitors in selected solvents

		Solubility in Water	Solubility in Acetone	Colour in solution	Solubility in Ethanol	Colour in solution	Solubility in Tetr/lene	Colour in solution	Solubility in White Spirit	Colour in solution
Photodegradation inhibitors	**A**	Insoluble	Readily soluble	Light yellow	Soluble	Transparent	Readily soluble	Yellow	Insoluble	Yellow sediment
	B	Insoluble	Readily soluble	Light yellow	Slowly dissolved	Transparent	Readily soluble	Yellow	Soluble	Transparent
	C	Insoluble at 1%. Water solubility at 0,1mg/lt at 20°C*	Very slowly dissolved in 1%. Insoluble at 2%	Yellow sediment	Insoluble	Yellow sediment	Readily soluble	Light yellow	Slowly dissolved leaving traces of yellow sediment	Light yellow
	D	Insoluble at 1%. Water solubility at 0,1mg/lt at 20°C*	Readily soluble	Transparent	Readily soluble	Transparent	Readily soluble	Transparent	soluble	Transparent
	E	Insoluble at 1%. Water solubility at 0,1mg/lt at 20°C*	Readily soluble	Transparent	Insoluble	Cloudy suspension	Soluble creating gel before dissolving	Transparent	Insoluble	-
	F	Insoluble	Readily soluble	Very light yellow	Insoluble	Cloudy suspension	soluble	Light yellow	Insoluble	-
	G	Insoluble	Readily soluble	transparent	soluble	transparent	Readily soluble	Light yellow	Insoluble	-
	H	Insoluble	insoluble	Yellow sediment	Insoluble	Yellow sediment	soluble	transparent	Insoluble	-
	I	Insoluble	insoluble	Yellow sediment	Insoluble	Yellow sediment	soluble	transparent	Soluble	Transparent

* Information given in the commercial data sheet of the product, provided by the manufacturing company

The newly prepared silk fabrics and threads were cut in different sizes according to the requirements of the tests to be performed. 2% solutions of inhibitors were prepared by dissolving 2 g of inhibitor in 98 ml solvent. In the case of the inhibitor combinations, 2% solutions were prepared using the same proportion of inhibitors from each category, 1 g of absorber and 1 g of hindered amine in 98 ml solvent.

The samples were immersed in a flat position in the inhibitor solutions and retained there for two minutes. For each sample a fresh solution was used every time. After immersion, they were removed and left to dry flat on Melinex sheet for 24 hours. All samples, fabric and threads were weighed before and after application of the compounds, in order to calculate how much additive was absorbed by the fibres. The weighing of the samples was done in a preconditioned laboratory room with temperature at 20°C and relative humidity at 35%RH (the absorption results can be found in *Appendix B, section B1*).

This application method selected was based on conservation strategies during solvent cleaning of historic textiles by immersion techniques. The textiles are soaked flat in specially made cabinets with fume extraction mechanisms. The solvent used is exchanged regularly to prevent soil redeposition and fresh solvent is used every time (Timar-Blazsy and Eastop 1998, 182). According to this, every sample was treated with new solution in order to avoid mixing of depositions. The drying process of solvent cleaned textiles for conservation purposes, presupposes the slow air drying in flat position for the safe evaporation of the solvent, in order to prevent pockets of fluid being trapped inside folds (Landi 1985, 93). This was exactly the case with the prepared and inhibitor treated samples, as it was noticed in preliminary tests, that if the samples were folded when soaked into the solutions, white marks were observed after drying due to the accumulation of the inhibitor in the folded areas. This is a disadvantage of the technique when dealing with large objects and those having linings and heavy decorations.

During the solvent evaporation the textile should be kept under controlled environmental

conditions in the fume chamber with relatively high relative humidity and low temperature to help the replacement of the organic solvent with water (Timar-Blazsy and Eastop 1998, 183). That is why the treated samples were left to dry under the operating fume chamber at constant room temperature in the chemical laboratory.

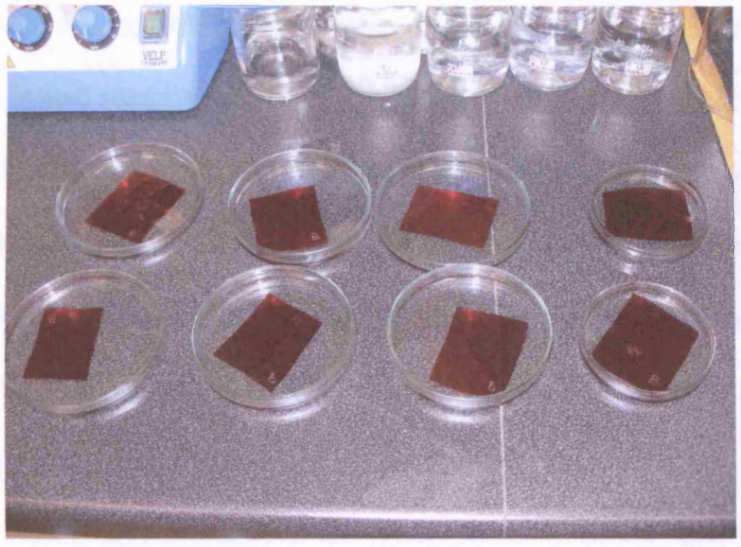


Figure 16. Silk fabric samples during treatment with inhibitor solutions

8.5.b Evaluation of application procedure

The application of the inhibitors to the new samples was of great importance. As the performance of these additives is evaluated for use on historic material, the method of application should be effective but also easy to perform and not dangerous to the object.

First of all the selection of solvent for the selected additives, which were all in solid form, was a major consideration from the conservation point of view. None of the selected additives was soluble in water. Water is a solvent usually preferred due to its ease of application, low cost and safety requirements. In the case of fragile historic textiles, however, the use of water is questionable. Fibres are hygroscopic materials and the introduction of water into their chemical structure is an irreversible and interventive treatment that should not be undertaken without a thorough investigation of the object (Timar-Blazsy and Eastop 1998, 194, 278).

The solubility of the additives in acetone was also considered, although inhibitor C (Tinuvin 327) was not soluble in this solvent, and as a result combinations H and I could not be created. Acetone is widely used in conservation applications, easily used in the laboratory and with low toxicity. On the other hand, it can dissolve some important components of textiles and it has to be used with due caution. It was observed in the pilot tests, using non dyed silk fabric samples that the treated samples dry very fast, because of the high volatility of the solvent. This may be an advantage on the one hand, because the overall treatment would take less time, but it is possible that the distribution and infusion of the photodegradation inhibitors into the fibres is not sufficient for light stabilization. It is known that when a solvent is a carrier of a material, such as the inhibitors tested in this research, its evaporation rate is important. If the solvent evaporates fast, the appropriate penetration may be inhibited (Torraca, 1975, 48).

After the preliminary tests, acetone can be considered a "strong" solvent on the selected additives, as four of them were readily soluble in it. A strong solvent is one that has a similar balance of intermolecular forces with the solute and therefore every solvent can be considered either strong of weak according to the solute used (Phenix, 1997, 4). As an example of this, acetone is a weak solvent for inhibitor C as it can dissolve very slowly only small quantities of the additive and cannot be used for higher concentrations needed. As far as toxicity is concerned, acetone is one of the least dangerous solvents and only in repeated and high exposure times may cause irritation problems to the eyes and dry the skin (Durrans, 1971,75, Timar-Blazsy and Eastop 1998, 180).

The use of ethanol solutions was also evaluated, although this time two of the selected inhibitors were not soluble in this solvent: inhibitor C and E and therefore inhibitor combinations F, H and I could not be created. An important observation on the solutions prepared with ethanol is that they are all colourless in contrast to the solutions prepared with the same inhibitors in other solvents and especially in tetrachloroethylene. This can be attributed to the possible creation of solvates by the additive and solvents other than ethanol after dissolution of the inhibitor. These

solvates have a light yellow colour in the case of other solvents. When ethanol is used either no solvates are present or they are colourless. This may be considered an advantage of this solvent as it may not affect the final colour of the textile when applied to it. This observation was subsequently investigated with colourimetric measurements of the treated non dyed samples in the pilot tests. In general ethanol worked as a medium to weak solvent with the selected inhibitors, as it needed more stirring time and slow addition of the additives to the solutions, in order to dissolve them. Ethanol solutions had a medium evaporation rate in comparison to the other solvents and its use in the laboratory was much easier. This is because the samples are drying reasonably fast without leaving any marks on the textile surface. Also the solvent is of low toxicity and with transient effects on humans, such as headache, fatigue, nausea and narcosis but this is only in long exposure times and 1400ppm atmospheric concentrations (Durrans, 1971, 79). On the other hand it is reported that some dyes used on textile objects may bleed with the use of ethanol. Dyed samples were not tested in this solvent in the context of this research.

White spirit is widely used in conservation applications. It is a commercial product from different manufacturing oil companies and it is available in different grades, according to the distillation range and aromatic content, which are important in the cleaning efficiency of the solvent when used in dry cleaning (Durrans, 1971, 103). In the present tests, low aromatic (or odourless) white spirit was used, which is mainly a synthetic product and more suited for use in the conservation laboratory. On the other hand its low evaporation rate is a disadvantage as the textile remains wet for a long period and this may cause swelling of some components, such as decorations or finishes of organic nature. Only three of the selected additives were soluble in white spirit: inhibitors B, C and D, and all of them were dissolved with difficulty in 2% concentration. It is interesting to observe that inhibitors that dissolved readily in other solvents do not dissolve in white spirit, with inhibitor A being an example of this. A second observation on the samples treated with white spirit was that samples treated with inhibitor C develop a white powder

crust on the fabric surface, suggesting that the additive was not absorbed by the fibres and was left on the surface after the evaporation of the solvent. It seems therefore that although white spirit is dissolving this additive it is incapable of introducing it into the fibres.

Tetrachloroethylene was the only solvent capable of dissolving all the selected inhibitors easily and fast. Combinations of inhibitors were also easily created and all additives were readily dissolved in this solvent at 2% concentration and also at concentrations up to 5%. Tetrachloroethylene is a widely used solvent in the dry cleaning of delicate textiles and it is considered a safe solvent for dyes and most other textile decorative materials. It was therefore chosen for the treatment of all the dyed samples used in this research.

A major disadvantage of tetrachloroethylene is its toxicity which is considered moderate to the eyes, gut, lungs and skin although it is not estimated as cumulative. It is considered the less toxic among other chlorinated hydrocarbon solvents and hazards are reported to users under long exposures of 100ppm (Durrans, 1971, 75). It is quite volatile and this feature is the cause of swill marks usually formed when drying (Landi 1985, 75). The volatility can sometimes be useful for conservation applications because objects can be dried quickly using warm air (Moncrieff and Weaver, 1996, 66). However, the problem with volatile solvents is that high concentrations can build up around the working area. They must therefore be used in a fume chamber and this makes their use less convenient and more appropriate for well equipped conservation laboratories and specialized staff

Since the toxicity of tetrachloroethylene was a major consideration, its possible replacement by a mixture of other solvents of low toxicity was investigated. In order to create such a mixture, the tested solubility of the additives in other solvents during preliminary testing was evaluated and the Teas solubility parameter system was used (*see Figure 17*). The solubility parameters of a solvent mixture can be estimated theoretically if the three solubility parameters of all its components are known (Torraca, 1975,50).

According to this system each individual solvent is assigned three numbers, F_d for the dispersion forces, F_p for polar forces and F_h for hydrogen forces. These numbers are plotted in a triangular diagram and those lying close to each other on the chart are expected to belong to the same group with similar solvent properties (Horie, 1987, 57, 57, Phenix, 1997, 4). When a solid additive is soluble in more than one solvent, the positions of these solvents in the Teas chart can give the expected solubility region of the material. Since all additives are readily soluble in tetrachloroethylene and at least one of the other chosen solvents, a binary mixture of two solvents (white spirit and acetone) could be created having the same solubility properties as tetrachloroethylene but with lower toxicity characteristics.

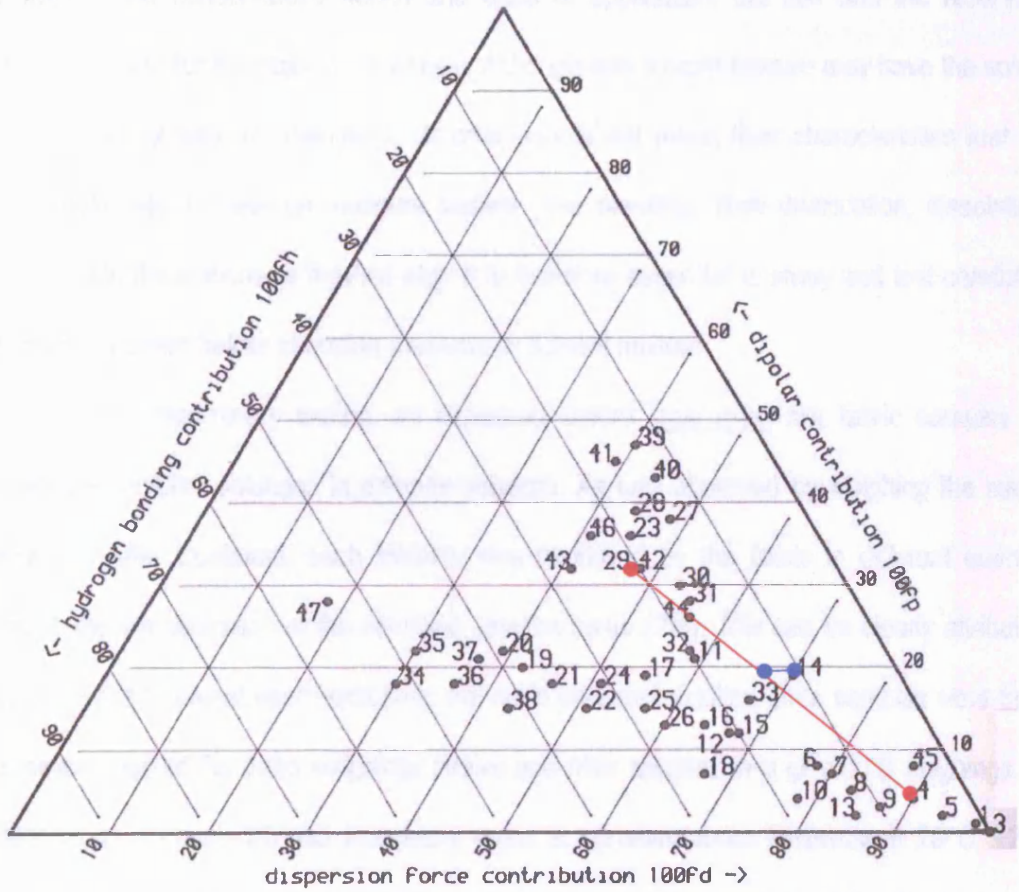


Figure 4.The TEAS Chart where the partial solubility parameters of the solvents are presented. The positions of the three selected solvents, tetrachloroethylene (14), acetone (29), and white spirit (4), are pointed (Horie, 1987, 186-194)

Using the Teas Chart, and noting the position of each of the two selected solvents and that of tetrachloroethylene in the chart, the proportion of each solvent in the mixture is calculated according to its parameters in comparison to the parameters of the given solvent (tetrachloroethylene) measured by the distance of their position in the chart. According to these calculations, a mixture having the same solubility properties as tetrachloroethylene could be prepared with 44% white spirit, 56% acetone. After preparing this mixture the solubility of all the inhibitors was examined. They dissolved readily in the mixture. This means that this mixture could replace tetrachloroethylene for the treatment of textile objects with photodegradation inhibitors for the sake of the conservator's health and ease of application, but still with the reservations expressed before for the object's sensitivity. Although this solvent mixture may have the solubility characteristics of tetrachloroethylene, its components still retain their characteristics that make them problematic for use on museum textiles (dye bleeding, fibre desiccation, dissolution of certain textile decorations or finishes etc). It is therefore essential to study and test carefully the object to be treated before choosing a solvent or solvent mixture.

During preliminary testing, as explained before, non dyed silk fabric samples were treated with inhibitor solutions in different solvents. As was observed by weighing the samples before and after treatment, each inhibitor was absorbed by the fabric in different quantities, although the concentration of the solutions was the same (2%). This can be clearly attributed to the action of the solvent used each time. For each prepared solution three samples were treated and the average of the three weighings before and after application is given. All weighings were performed in a preconditioned laboratory room at constant room temperature 20°C ±2 and relative humidity 35%RH. The exact measurements are presented in tables in *Appendix B, section B.1.1 and B.1.2.*, while the averages and standard deviation of the measurements are presented in Table 21.

Table 21. Percentage absorption averages of the additives by the silk fabric through different solvent solutions

solvent		**Acetone**		**Ethanol**		**Perc**		**White Spirit**	
		%absorb	St. Dev.	%absorb.	St. Dev.	%absorb.	St. Dev.	%absorb	St. Dev.
Inhibitor treated samples	**A**	8,89	0,6	5,99	1,0	6,77	0,5	-	
	B	9,91	0,3	7,41	1,2	6,89	0,2	7,18	0,3
	C	-		-		8,10	0,5	7,22	5,2
	D	10,31	0,5	7,14	0,8	8,99	0,8	6,76	1,5
	E	11,19	0,7	-		11,34	1,4	-	
	F	9,59	0,5	-		11,72	2,8	-	
	G	8,79	0,3	7,78	0,3	8,48	1,4	-	
	H	-		-		14,52	3,9	-	
	I	-		-		14,76	7,3	6,90	1,1

After examining the graphs showing the % absorption of each inhibitor (an example is given in Figure 18, and all the charts are presented in *Appendix B, section B1.5),* it is concluded that:

Inhibitor A is better absorbed by the fabric when an acetone solution is used. The same is observed with inhibitor B which belongs to the same category of inhibitors as A (benzophenone absorbers). Inhibitor C (benzotriazole absorber), on the other hand, is only soluble in two solvents (tetrachloroethylene and white spirit) showing its maximum absorption when samples are treated with tetrachloroethylene solution. It was also noticed, as mentioned above, by macroscopic investigation, that this inhibitor forms a powder crust after the evaporation of the solvent, meaning that the additive was not properly absorbed and retained by the fibres after application.

Inhibitor D gives its highest absorption when applied in acetone solution, while tetrachloroethylene has also a high percentage. Samples treated with Inhibitor E, on the contrary, absorb more additive when it is dissolved in tetrachloroethylene than in acetone.

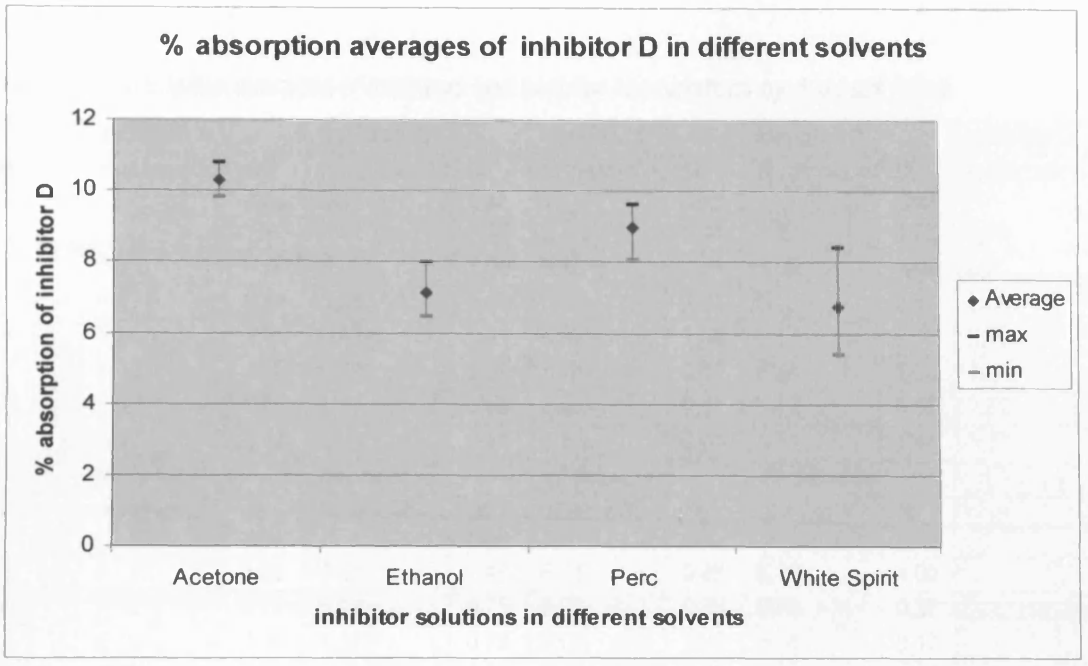


Figure 18. Graph showing the % absorption-average of inhibitor D when dissolved in different solvents

As an overall conclusion, tetrachloroethylene and acetone proved to provide the better absorption of the inhibitors by the textile fibres, with the advantage given to tetrachloroethylene because all the selected additives are soluble in it.

As pointed before, all dyed silk fabric and thread samples were treated with inhibitors using a tetrachloroethylene solution. Table 22 shows the average % absorption of inhibitors and inhibitor combinations by the silk fabric dyed with different dyes and dye combinations. Likewise, Table 23 shows the average % absorption of the treated thread samples (tables of all weightings are given in *Appendix B, sections B1.6 and B1.7*).

Table 22. % absorption averages of inhibitors and inhibitor combinations by dyed silk fabric

	Inhibitor A		**Inhibitor B**		**Inhibitor C**		**Inhibitor D**		**Inhibitor E**	
Dyed samples	*% Absorb.*	*St. Dev.*	*% Absorb.*	*St. Dev.*	*% Absorb.*	*St. Dev.*	*% Absorb.*	*St. Dev.*	*% Absorb.*	*St. Dev.*
Madder	6,07	1,53	6,51	0,92	6,28	1,44	6,12	0,72	7,15	1,35
Brazilwood	5,89	1,89	6,07	1,65	5,10	1,38	6,06	1,64	6,71	1,05
Safflower	5,11	0,81	5,84	1,48	3,85	2,23	5,10	0,51	5,85	1,45
Cochineal	4,50	1,29	4,47	1,11	4,92	1,08	5,17	1,17	6,76	0,94
Comb.1	5,54	1,35	5,99	0,98	5,64	0,67	6,38	1,00	10,40	7,19
Comb.2	5,57	1,85	7,11	0,69	6,47	0,37	6,12	0,55	7,52	0,25
Comb.3	5,06	0,44	4,84	0,11	4,85	0,61	5,63	1,44	5,71	0,37
	Inhibitor F		**Inhibitor G**		**Inhibitor H**		**Inhibitor I**			
	% Absorb.	*St. Dev.*	*% Absorb.*	*St. Dev.*	*% Absorb.*	*St. Dev.*	*% Absorb.*	*St. Dev.*		
Madder	8,82	1,58	4,57	1,40	6,71	0,89	6,20	1,60		
Brazilwood	5,63	0,21	6,08	0,75	6,80	0,30	5,98	0,27		
Safflower	6,11	0,78	5,36	0,78	6,69	2,00	5,04	0,17		
Cochineal	6,37	2,94	4,35	1,87	6,42	1,03	5,41	1,15		
Comb.1	6,32	2,10	6,95	1,17	7,48	1,76	6,90	1,23		
Comb.2	6,65	1,27	6,33	0,35	7,81	1,11	6,32	0,46		
Comb.3	5,80	0,49	5,54	0,46	6,24	0,94	5,83	1,31		

Table 23. % absorption averages of inhibitors and inhibitor combinations by dyed silk threads

	Inhibitor A		**Inhibitor B**		**Inhibitor C**		**Inhibitor D**		**Inhibitor E**	
Dyed samples	*% Absorb*	*St. Dev.*	*% Absorb*	*St. Dev.*	*% Absorb*	*St. Dev.*	*% Absorb*	*St. Dev.*	*% Absorb*	*St. Dev.*
Madder	12,27	1,23	12,48	2,49	11,03	0,52	13,18	1,69	12,12	2,58
Brazilwood	14,91	3,91	15,66	3,14	14,27	0,73	14,62	2,59	17,11	2,02
Safflower	14,80	0,79	13,43	2,01	12,35	1,89	14,27	1,06	16,40	1,77
Cochineal	13,25	2,85	13,57	2,03	12,70	1,24	11,34	5,25	16,74	6,97
Comb.1	12,15	1,97	13,23	2,89	12,83	4,02	12,76	3,54	13,80	0,78
Comb.2	11,50	1,08	12,03	5,08	8,93	4,55	12,09	1,08	12,13	2,79
Comb.3	15,47	3,18	14,28	3,94	13,70	5,22	14,72	1,30	14,36	2,60
	Inhibitor F		**Inhibitor G**		**Inhibitor H**		**Inhibitor I**			
	% Absorb	*STDEV*	*% Absorb*	*STDEV*	*% Absorb*	*STDEV*	*% Absorb*	*STDEV*		
Madder	12,14	1,99	10,19	0,84	10,57	0,65	10,67	1,82		
Brazilwood	15,17	0,86	15,90	4,02	21,24	5,62	16,99	1,68		
Safflower	17,41	8,32	15,01	1,90	18,29	1,09	15,83	2,09		
Cochineal	12,87	0,87	11,11	2,18	13,62	3,00	13,06	0,26		
Comb.1	11,51	2,46	11,41	0,41	13,38	1,79	11,09	2,26		
Comb.2	10,71	1,50	12,19	0,67	14,36	0,87	13,20	2,71		
Comb.3	13,90	0,49	14,17	0,40	18,36	3,06	15,49	1,30		

It is evident that the absorption of the additives by single threads was much higher than by the fabric. This may be due to the thickness of the threads and possibly their twist, which make them absorb and retain the additives within their structure. This observation must be taken into consideration in the case of embroidered textile objects, where the background fabric with plain weave may absorb much less inhibitor than the embroidered parts of the object.

By the study of these results, it can be observed that the absorption of inhibitors by the silk fibres is dependent both on the type of inhibitor and inhibitor combination, the selected solvent and the dyestuffs and dye combinations present on the fibres. In general Inhibitor E and inhibitor combinations F and H showed the higher absorption levels on all dyed samples. Inhibitor E is Chimassorb 944 and both F and H contain Chimassorb 944 in combination with two other additives. This leads us to the conclusion that Chimassorb 944 is generally better absorbed and retained by the silk fibres than the other additives. Also samples dyed with the dye combination 1, brazilwood, madder and tannin had the highest up-take of all the dyed samples, showing again the highest % absorption with inhibitor E, Chimassorb 944.

Section Summary

The preparation of the new sampling material was based on the identification of historic samples taken from Greek Museums. New samples were prepared from natural *bombyx mori* silk fabric and embroidery threads, dyed with traditional methods with selected natural dyes and dye combinations found on historic samples. The authenticity of the new sampling material was evaluated by comprehensive fibre identification using solubility and microscopic methods and high performance liquid chromatography for the identification of the dyestuffs used.

After due investigation using bibliographic references, market research and pilot tests, five photodegradation inhibitors were finally selected for light fastness testing. Four inhibitor combinations were also chosen for further testing in order to examine a possible synergetic effect between them.

The newly prepared sampling material was treated with the selected inhibitors and inhibitor combinations in solvents commonly used in textile conservation. After evaluating the performance of the solvents, the method of application, the concentration of the solutions and the changes induced in the textile specimens through pilot tests, the dyed silks were treated with the selected inhibitors in a 2% tetrachloroethylene solution.

9. Evaluation of treated samples

According to the objectives of this study the prepared samples of silk fabric need to be evaluated, after treatment with inhibitors and before any exposure to electromagnetic radiation, in order to understand the effect caused by the treatments to their construction materials, fibres and dyes. Any changes induced by the application of inhibitors (other than changes in light stability) may be considered negative and side effects such as changes in colour or mechanical properties will discourage their use on museum textiles. Removability of the additives is also considered and evaluated.

9.1 Colour change evaluation

9.1.a Instrumental colour evaluation

Colour changes on all samples after treatment were measured with instrumental colourimetry. The basic description of the colour is given primarily by the CIE system, from the initials of the "Commission Internationale de l' Eclairage" (International Commission on Illumination). According to this system any colour is perceived by its three dimensions, hue, chroma and lightness. These three terms are basically describing the dimensions of a colour as this is perceived by a normal human observer (Johnston-Feller 2001, 20). In order to have two colours matching these three quantities must be identical (Johnston-Feller 2001, 24). The three quantities are called tristimulus values X, Y (lightness) and Z as determined from CIE. Any colour therefore can be expressed as the sum of the relative amount (*x,y,z)* of these three values and these amounts are called *chromaticity coordinates*. To help in the visualization of the tristimulus values the CIE system defines the three chromaticity coordinates (*x,y* and *z*) derived from the three tristimulus values by the following equations:

$$x = \frac{X}{X+Y+Z}$$

$$y = \frac{Y}{X+Y+Z}$$

$$z = \frac{Z}{X+Y+Z}$$

These coordinates represent the hue and chroma of a colour and the first two of them (*x* and *y*) give the chromaticity diagram established by the CIE system, given in Figure 19. The third coordinate *z* is only completing the sum $x + y + z = 1$ and it is not recorded in the diagram.

Figure 19.The CIE chromaticity diagram showing the wavelength of various colours (after Johnston- Feller, 2001, 27)

Since the two coordinates cannot describe a colour completely, a lightness factor(Y) must also be included to identify the colour precisely. In the CIE colour system, the tristimulus value Y is used as a lightness factor expressed as a percentage based on a perfect reflectance of 100%. The lightness Y can be seen as being placed perpendicular to the level surface of the chromaticity diagram *(see Figure 20).*

To measure the differences between two colours there are three different equations. The total colour difference (magnitude of the colour difference) is expressed as ΔE, the difference due only to chromaticity differences as ΔC, and the difference in lightness as ΔL.

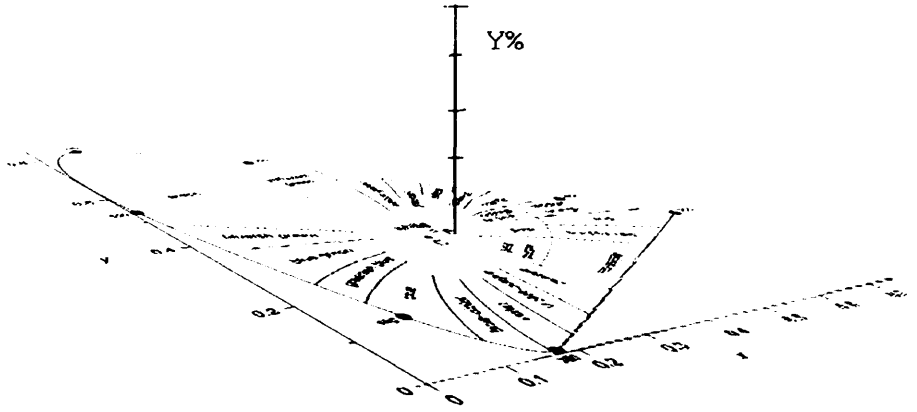


Figure 20. The CIE chromaticity diagram and the lightness Y

The most recommended difference equation by the CIE system is referred as CIELAB using the *L* a**and *b** coordinates, which can be calculated from the tristimulus values X,Y and Z: *L** for lightness, *a** for redness-greenness and *b** for yellowness-blueness. These coordinates can be represented as two perpendicular axes for a* and b* while L* is perpendicular to the plane formed by a* and b* and intersects it at the neutral point.

The differences in colour between a treated or aged sample 1 and the reference blank sample 2, may be resolved into individual components, which indicate the direction of the difference:

$\Delta a^* = a^*_1 - a^*_2$ → positive = redder; negative = greener

$\Delta b^* = b^*_1 - b^*_2$ → positive = yellower; negative= bluer

$\Delta L^* = L^*_1 - L^*_2$ → positive = lighter; negative = darker

The ΔL^*, Δa^* and Δb^* represent the difference between the L*,a* and b* values before and after treatment or exposure to electromagnetic radiation and the magnitude of the colour difference (ΔE) is given by the equation:

$$\Delta E = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2}$$

The CIE system recommends this equation because it can be computed easily and because its standard usage helps to decrease the confusion and misunderstandings (Johnston-Feller 2001, 34).

9.1.b Colour change evaluation of treated samples

The next step for the evaluation of the application of inhibitors to the newly prepared samples was to check if there was a colour difference after treatment. This was firstly evaluated in the pilot tests by eye examination of the treated samples and then by colorimetric measurements. For samples used in the pilot tests which were all non dyed silks, colour evaluation was performed by colourimetric measurements with the use of a *Spectro-color* colourimeter with light source D65, a 3mm diameter measuring area, and a 10° illumination angle. The meter was calibrated before each measuring session using standard white and black plates. For these measurements the CIE

L*a*b* system was used.

It was noticed that although treated samples show little or no noticeable colour change by eye examination, there are some noticeable colour changes measured with the given equipment. For each set of samples, three measurements were taken in different areas of the same sample and ΔE, ΔL*, Δa* and Δb* values were calculated. The averages of these measurements and their standard deviation are given in Table 24 (all measurements can be found in *Appendix B2.)*

Table 24. Colourimetric measurements - averages on treated with inhibitors non dyed samples in different solvents

Treated samples in Acetone	**Av. ΔL***	**Av. Δa***	**Av. Δb***	**Av. ΔE**	**Standard Deviation of ΔE**
Inhibitor A	0,09	-0,78	2,03	**2,18**	0,3
Inhibitor B	-0,08	-0,78	1,97	**2,12**	0,4
Inhibitor D	-0,27	-0,09	1,16	**1,20**	0,2
Inhibitor E	-0,64	-0,12	1,40	**1,54**	0,2
Inhibitor F	-0,72	-0,57	2,64	**2,80**	0,2
Inhibitor G	-0,56	-0,38	7,61	**2,02**	0,5
Treated samples in Ethanol					
Inhibitor A	-0,09	-0,58	1,14	**1,28**	0,3
Inhibitor B	-1,32	0,61	0,14	**1,46**	1,5
Inhibitor D	-0,49	-0,29	0,82	**1,00**	0,2
Inhibitor G	-0,53	-0,24	1,50	**1,61**	0,4
Treated samples in Tetrachloroethylene (Perc)					
Inhibitor A	-0,39	-0,41	1,85	**1,94**	0,2
Inhibitor B	-0,30	-0,58	2,04	**2,14**	0,4
Inhibitor C	-0,08	-2,04	5,15	**5,54**	0,3
Inhibitor D	-0,34	-0,46	1,83	**1,92**	1,3
Inhibitor E	-0,08	-0,46	1,78	**1,84**	0,5
Inhibitor F	-0,07	-0,59	1,60	**1,71**	0,1
Inhibitor G	0,19	-0,75	1,75	**1,91**	0,4
Inhibitor H	-0,47	-1,55	4,87	**5,13**	0,9
Treated samples in White Spirit					
Inhibitor B	-0,18	-0,33	1,57	**1,62**	0,4
Inhibitor C	-0,32	-0,62	2,51	**2,61**	0,5
Inhibitor D	-0,36	-0,13	1,94	**1,98**	1,1
Inhibitor I	-0,38	-1,19	4,10	**4,29**	0,2

By studying the values given in the above table and having in mind the information pointed out earlier, it is observed that all the non-dyed samples became yellower after the application of inhibitors, as all Δb* values are positive. This observation was also slightly apparent by eye examination. It can also be noticed that most of the treated samples became darker after

the application of photodegradation inhibitors giving negative results in ΔL* values.

What can be observed by the elaboration of the measurements and the creation of relevant graphs is that the overall colour changes of the treated fabrics are dependent not only on the inhibitors used, but also on the solvents used with the same inhibitor. As a general observation, inhibitor C, wherever dissolved, causes the maximum colour change, while inhibitor D shows the minimum.

It is important to give attention to the induced colour changes on each set of samples treated with the same inhibitor but through different solvent solutions. It was obvious, as already foreseen by previous evaluation of the prepared solutions, that silk samples treated with inhibitors that were soluble in ethanol showed the least colour difference after application. As said before, all solutions prepared in ethanol were colourless, while solutions of the same inhibitors prepared for example in tetrachloroethylene were yellow or light yellow. This may be an advantage of the use of ethanol, as the minimum change in the colour of an object is always preferable. An example of the colour changes after treatment with inhibitor D in 2% solution in different solvents is given in Figure 21. The rest of the graphs showing the colour changes of all treated samples with inhibitors dissolved in different solvents are presented in *Appendix B2.5.* Each column in the graph represents the overall colour change (ΔE) after treatment in different solvents. The higher the column, the more colour change induced in the non dyed silk sample after treatment.

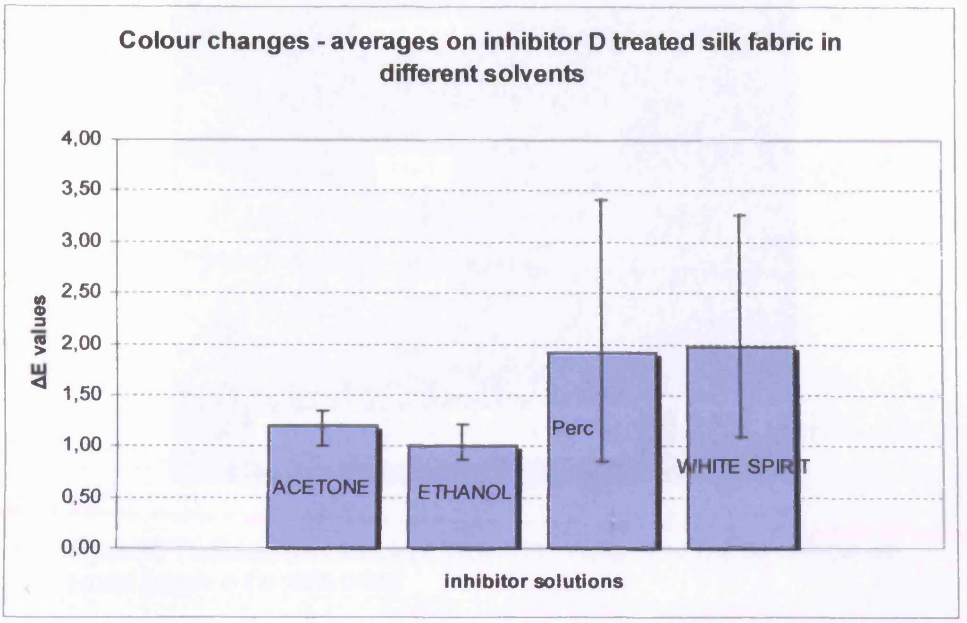


Figure 21. Colour changes-averages measured on silk fabric samples treated with inhibitor D using solutions of different solvents. The error bars show the range of three measurements

Samples dyed with natural dyes and dye combinations were all treated with the selected inhibitors and inhibitor combinations in tetrachloroethylene. Their colour change after treatment was checked at first by eye, where there was no noticeable change of colour on the treated samples in comparison to the non treated ones. This can be confirmed by photographic records of the treated and blank samples. A characteristic photograph can be seen in Figure 22, where the samples dyed with cochineal and treated with inhibitor A (2-hydroxy-4-methoxybenzophenone) are presented. The sample on the top is the non treated (blank) sample while the three samples in the bottom are the inhibitor-treated samples. As one can observe macroscopically there is little or no change in colour after application.

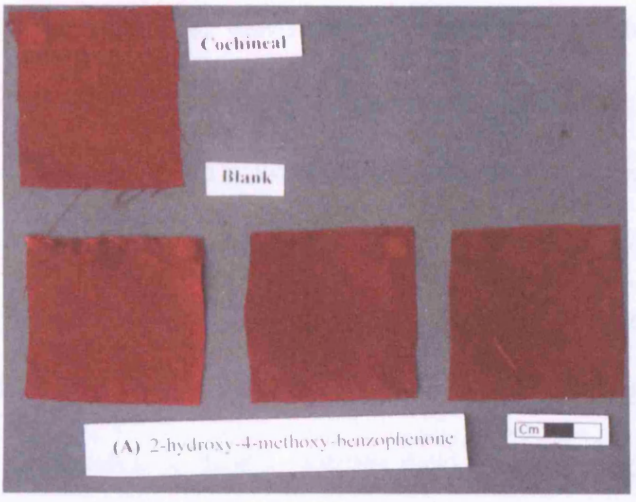


Figure 22. Textile samples after application of an inhibitor in comparison with the non treated sample in the same colour

Colourimetic measurements were performed on the treated samples in order to evaluate if there were any quantitative changes in colour after treatment with inhibitors. The colour change evaluation was performed by colourimetric measurements with the use of a Minolta CR-221 chromameter with light source C, a 3mm diameter measuring area, and a 45° illumination angle. The meter was calibrated before each measuring session using a standard white plate. Three measurements were taken from each treated sample and were compared to the non treated sample measurements taken before. The magnitude of the colour difference (ΔE) was calculated and relevant charts were prepared (*see Appendix B, section B.2.15)*. By the study of these charts it is apparent that even though, to the eye, the samples after treatment show no colour changes, in fact there were some noticeable changes not only according to the inhibitor used but to the dyes and dye combinations used respectively.

In all cases, madder dyed silks are the most affected by any treatment with inhibitors or inhibitor combinations as their colour have changed noticeably. The same is also noticed in samples dyed with dye combination 2 which contains madder and shows significant colour change after the application of any of the selected inhibitors. On the other hand this is less the case with the samples dyed with combination 1, which also contains madder. The next most

affected samples were the ones dyed with safflower. These samples show significant colour change after treatment but the change is not very dependent on the additive.

The least affected samples are those dyed with cochineal. They have almost negligible colour change in most of the cases, with the exception of inhibitor C, which is still low. Good performance is also observed on samples dyed with combination 3, which consists mainly of cochineal. These samples show little colour change after treatment in comparison to others dyed with madder and dye combination 2. Finally, samples dyed with brasilwood undergo a medium colour change, although this is different for every additive applied.

From the above, it can be observed that fabrics dyed with dark shades, dark red for cochineal and violet red for combination 3, are less affected by inhibitor treatment as their colour had hardly changed. On the other hand, lighter shades such as the salmon pink safflower and the dull orange madder, show significant colour changes after the addition of inhibitors. Still, safflower dyed samples, which have the lightest colour of all, are not showing the highest colour change. In Figure 23, a representative chart is given derived from colourimetric measurements to samples after treatment with inhibitor D. Each column represents a different dye or dye combination. The longer column in given by a light shade (safflower) meaning the higher colour difference, while a darker shade (cochineal) shows the minimum colour change after inhibitor application (relevant charts for all the rest samples are presented i*n Appendix B, section B2.15*).

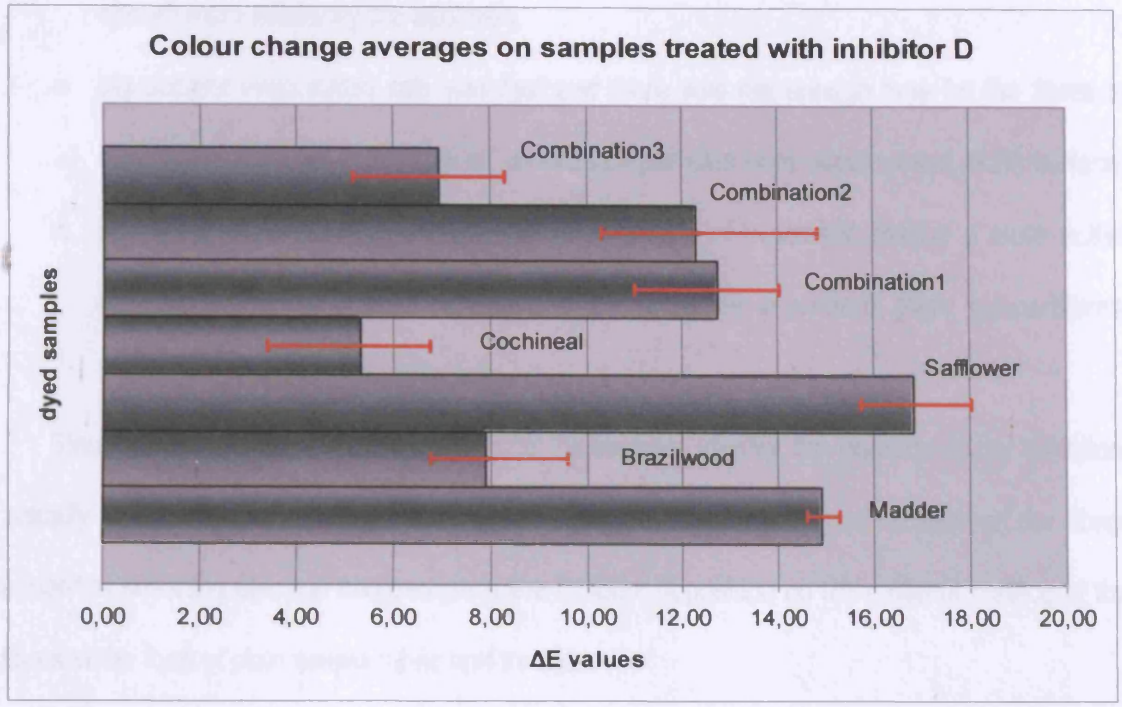


Figure 23. Chart showing the colour difference averages measured on samples after treatment with inhibitor D. The error bars show the range of three measurements

9.2 Macroscopic and microscopic evaluation of the treated samples

After treatment with the inhibitors, the samples were investigated using the scanning electron microscope in order to examine possible changes in surface morphology (*all images are given in Appendix B.3*).

The samples were examined at two basic magnifications for the fabric, at ×100 where the overall structure of the weave is visible and at ×500 where isolated fibres can be examined in detail. As for the treated threads, magnifications of ×400 and ×1200 were generally selected in order to closely examine the surface of the treated fibres.

What was observed in general is that, even if additives are thought to be absorbed by the fibres, their presence is clearly evident on the surface of the fibres in the form of amorphous crystals, oblong particles or shapeless film. This may be due to several reasons:

- the concentration used was rather high for complete absorption by the fibres;
- the use of the selected organic solvent did not help the swelling of the fibres in order to

absorb more efficiently the additives;

- the solvent evaporation rate was fast and there was not enough time for the fibres to absorb the additives in the interior, so inhibitor particles were accumulated at the surface;
- the application method was deficient for this kind of treatment; maybe a more active method should be used, for example a dyeing-like procedure (high temperatures, intermixing, addition of auxiliaries).

Since there was no available method to measure or identify the quantity of the inhibitors actually absorbed by the fibres, what can be observed by the close examination of the fibres under the scanning electron microscope is the inhibitor deposition on the external surface of the fibres in the form of plain weave fabric and threads.

No differences are observed in the different dyed samples but in different inhibitors. Inhibitor A which is an absorber (2-hydroxy-4-methoxy-benzophenone) seems to present the most successful absorption by the fibres in the silk fabric regardless of the dyestuff used. It is not usually visible on the surface of the fibres and if so, it is present in the form of crystal incorporations. In the case of silk fibres in threads, larger crystals are manifested. Examples of that can be seen in Figure 24, where three samples are presented dyed with different dyestuffs, two coming from silk fabrics and one from the silk threads, and treated with inhibitor A.

Figure 24. Samples of fabric and thread treated with inhibitor A *(2-hydroxy-4-methoxy benzophenone)* during SEM examination

The application of inhibitor B which is also an absorber (2-hydroxy-4-n-octyloxy benzophenone) to fabric and threads had as a result the deposition of bigger crystals in the external fibre surface that can be detected even in lower magnification and they are even visible in the external view of the weave. Examples of samples treated with inhibitor B are given in Figure 25.

Figure 25. Samples of fabric and thread treated with inhibitor B *(2-hydroxy-4-n-octyloxy benzophenone)* during SEM examination

Inhibitor C, an absorber of benzotriazole type (Tinuvin 327), shows a completely different appearance when accumulated in the external surface of the silk fibres. Oblong, fibrous tiny particles uniformly cover the cylindrical surface of the fibres and they can be seen as particles of dust in lower magnifications, while at higher magnification it is apparent that they are spread around the fibre. Examples of these observations are shown in Figure 26, where three differently dyed samples at three magnifications are presented.

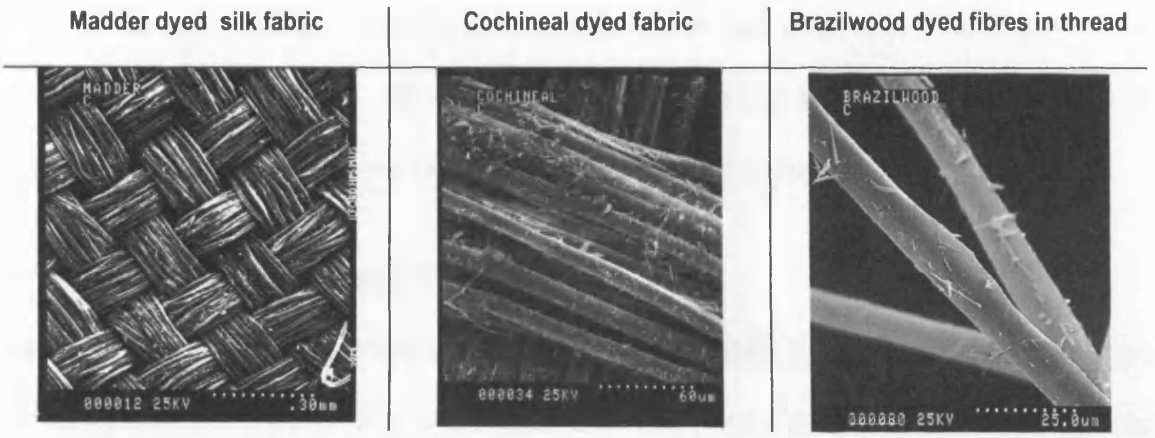


Figure 26. Samples of treated fabric and thread with inhibitor C (Tinuvin 327) during SEM examination

Inhibitors D and E, both belonging to the antioxidant class and being both hindered amines (HALS) have generally the same view when applied to silk fibres and examined in the SEM. They are rather more absorbed by the fibres than the other inhibitors presented before, but still in many cases amorphous crystals of the additives are accumulated in groups on the surface of the fibres. Two examples are given in Figures 27 and 28 while full photographic documentation of all the treated samples is given in *Appendix B3.*

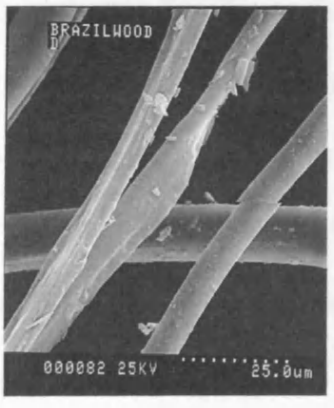


Figure 27. Brazilwood dyed silk fibres in threads treated with inhibitor D (Tinuvin 770) in magnification X1.20k during SEM examination

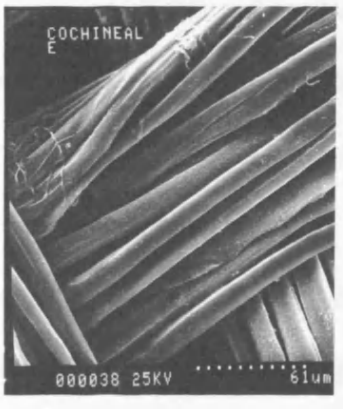


Figure 28. Cochineal dyed silk fabric treated with inhibitor E (Chimassorb 944) in magnification X500 during SEM examination

The samples treated with inhibitor combinations show similar external surface views as the ones described above, according to the inhibitors that were used each time. In general the additive particles accumulate less at the fibre surface, probably because the concentration of each additive was lower (1%) and this helped in the overall absorption.

9.3 Testing of mechanical properties

The mechanical properties of the silk fibres after the application of the inhibitors ought to be tested for the complete evaluation of the treatments. Ideally, the mechanical properties should not be changed, in order for a treatment to be suitable for conservation purposes.

The mechanical properties of natural fibres are reduced by ageing and also by several chemical treatments during manufacturing, cleaning during useful life or previous conservation applications. It is not permissible to cause extra reduction of the mechanical properties by treatment with photodegradation inhibitors.

The mechanical properties in question are tensile strength and elongation. Tensile strength is with other words the breaking strength of the fibre measured by the force needed to break the fibre, and it is expressed by force per unit of cross-sectional area. The tensile properties of fibres are closely related to the environmental conditions present and are significantly reduced when the textile is wet. Elongation is a parameter characterizing the stretching properties of the treated fibres when a force is induced. It is measured by the percentage increase in length in relation to the original length. It is usually expressed either by the elongation reached when the fibre breaks or the elongation under a particular load.

For testing these two parameters, a tensile test was performed on non-dyed silk treated with inhibitors, based on a standard method ISO 13934-1:1999(E), Part 1: Determination of maximum force and elongation at maximum force using a strip method.

9.3.a Preparation of samples and testing method

New silk fabric samples were cut into strips of 200mm length and 50mm width (excluding the fringe). Ten samples were cut for the needs of each set, five from the warp direction of the fabric and five from the weft (*see Figure 29*). In reality the samples were cut a little larger than the above mentioned dimensions specified by the standard method (aprox.70mm width). This was because, after treatment with inhibitors and inhibitor combinations, threads were removed in equal numbers from each of the long edges, in order to achieve the specified width (50mm). The total number of samples tested was 100.

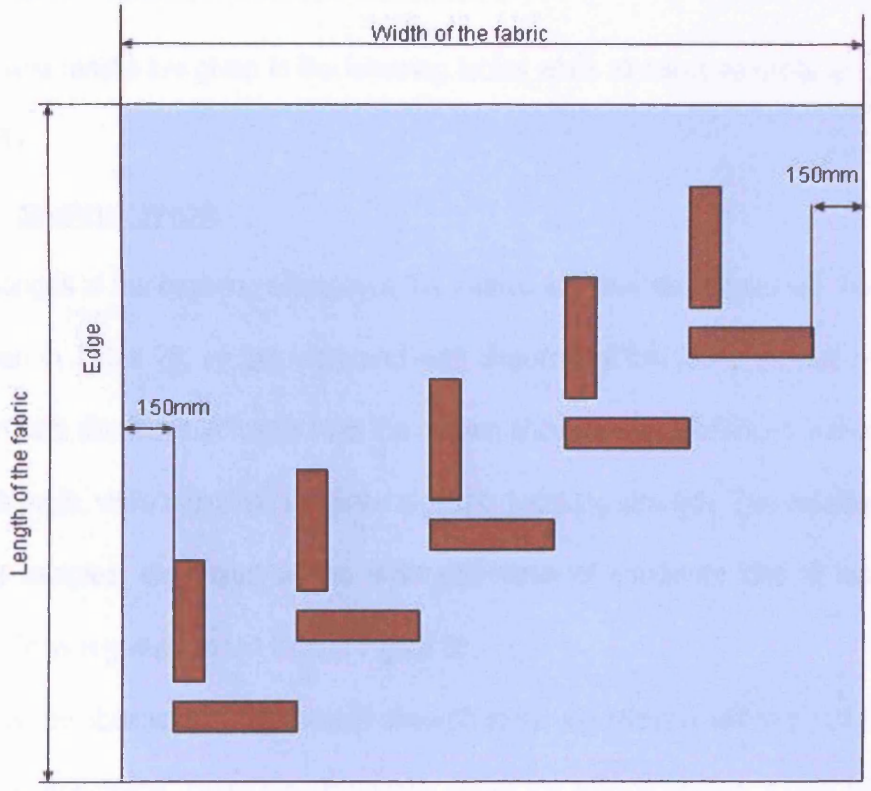


Figure 29. Locations of the silk samples cut form the whole textile as specified by ISO 13934-1:1999(E)

After cutting the samples, they were treated with the nine selected inhibitors and inhibitor combinations in solutions of 2% in tetrachloroethylene. After treatment the samples were

preconditioned, flat in a relaxed state, for 24 hours in a specialized laboratory room with environmental conditions, 20°C temperature and 65%RH as specified by standard EN20139.

The apparatus used for the tensile testing is a constant rate of extension (CRE) machine, SDL Universal tensile tester-UTT350, with gauge length 200mm, constant rate of extension 100mm/min and pre-tension of the samples 2N. During the test, the maximum load at rupture in Newtons was recorded along with the extension of the samples in millimeters at maximum load and elongation in percent at maximum load.

9.3.b Results of mechanical tests and evaluation

Representative results are given in the following tables while all measurements are presented in *Appendix B4.*

Changes in breaking strength

Several changes in the breaking strength of the treated samples were detected. These changes can be seen in Table 25, on the warp and weft direction of the fabric as well as the *overall change*[27].in both directions. A minus (-) in the column showing the % changes, indicates a loss in breaking strength, while a plus (+) indicates a gain in breaking strength. The breaking strength of the treated samples, expressed as the arithmetic mean of maximum load at rupture in both weave directions is given in chart form in Figure 30.

It can be observed that the tensile strength of the silk fabric is affected by treatment both positively and negatively. There are also cases where the overall change is very small (-0,87%) and can be considered negligible, as in the case of inhibitor C, meaning that this inhibitor is not changing significantly the tensile properties of the silk fabric. The Student's *t*-test performed for this set of samples at 1% significance level gives *t=0,705* and changes in breaking strength are not statistically significant, with *P=0,50.*

[27] *Overall change* is defined as the average of all measurements in the warp and weft direction

In the case of mechanical testing, a 0,01level of significance (1%) was selected in all cases as more conservative, meaning that there is only one chance in a hundred of being wrong and we are therefore 99% confident that the effect is genuine (Morgan 1991, 7): the null hypothesis (there is no change in mechanical properties of the treated silks) is rejected or not on this basis.

Table 25. Maximum load averages of treated with inhibitor silks and per cent change in breaking strength, in comparison to the non treated sample

	WARP			WEFT			
Treated samples	**max load (N)**	**St. Dev**	**% change**	**max load (N)**	**St. Dev**	**% change**	**Overall % change in breaking strength**
BLANK	209,4	1,48		319,7	9,63		
Inhibitor A	206,4	5,20	**-1,4**	317,3	10,01	**-0,7**	**-1**
Inhibitor B	200,1	3,83	**-4,5**	313,9	2,72	**-1,8**	**-2,9**
Inhibitor C	206,2	5,78	**-1,6**	318,4	10,44	**-0,4**	**-0,9**
Inhibitor D	188,3	14,72	**-10,1**	316,4	7,9	**-1**	**-4,6**
Inhibitor E	205,8	5.04	**-1,8**	336,7	13,54	**5,3**	**2,5**
Inhibitor F	208,9	1,84	**-0,3**	344,5	10,79	**7,8**	**4,6**
Inhibitor G	195,5	2,78	**-6,7**	324	10,51	**1,3**	**-1,8**
Inhibitor H	203	7,93	**-2,6**	350,5	15,10	**9,6**	**4,7**
Inhibitor I	198,9	2,83	**-5,1**	324,8	8,74	**1,6**	**-1**

At the same time it is noticed that some treatments increase the breaking strength of the treated fabric, like inhibitor H showing an increase of the overall change of +4,78%. However, Student's *t*-test shows (at 1% level of significance) that the improvement of breaking strength after treatment with inhibitor H is not significant (*t=-2,63* and *P=0,030).*

As breaking strength is usually negatively affected by photodegradation, an improvement of this mechanical property is welcomed and sometimes aimed for by the addition of stabilizing materials. The endorsement of textile fibres which results in improvement of breaking strength is important during handling of museum textiles and especially when objects need to be hung for display. For example, in the case of heavy embroidered ecclesiastical vestments which include

metal thread decorations, attached to a sensitive silk background, the resistance of the silk fibres to mechanical forces due to the added weight is vital.

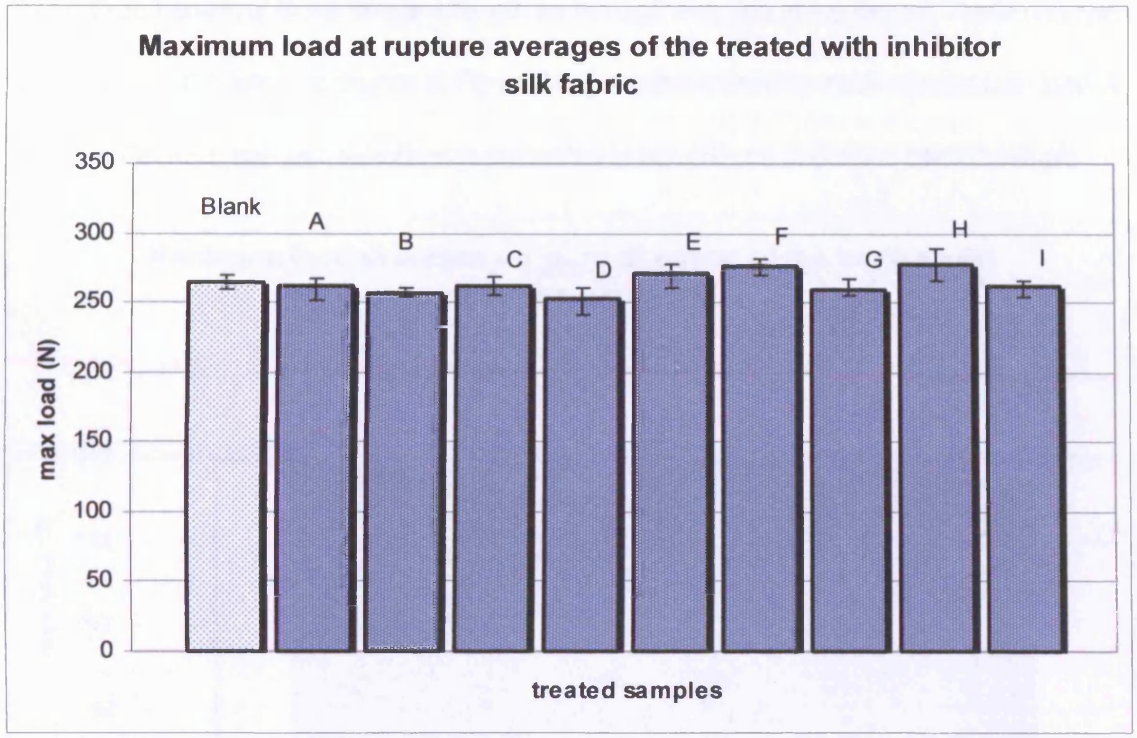


Figure 30. Overall change on maximum load at rupture of the treated with inhibitors and inhibitor combinations silk fabric in comparison to the non treated sample.

On the contrary there are treatments, like the ones with inhibitors A, B, D, G and I which reduce the breaking strength. The maximum negative change is given by inhibitor D (-4,63%) and this could be seen as a disadvantage of the particular additive. However, the *t*-test gives *P=0,034* showing that this result is not statistically significant at significance level of 1%.

A decrease in breaking strength means that the object will be more sensitive during handling and less able to withstand its own weight during several display methods. If this is the case, most of the times fragile textile objects are stored or displayed flat and with appropriate support at all times regardless of their original shape, or use (e.g. flags).

On the other hand, if Table 25 is studied in detail, one can see that changes in breaking strength vary according to the weave direction. It is noticed that in all cases the warp direction of

the fabric is negatively affected by the application of inhibitors, although the change caused by combination F is very low (-0,32%) On the contrary, more than half the inhibitor treatments proved to be beneficial to the tensile strength on the weft direction of the weave. These changes can be seen in the following graphs of Figure 31 where the arithmetic mean of maximum load at rupture in the warp and weft directions is presented in comparison to the non treated sample.

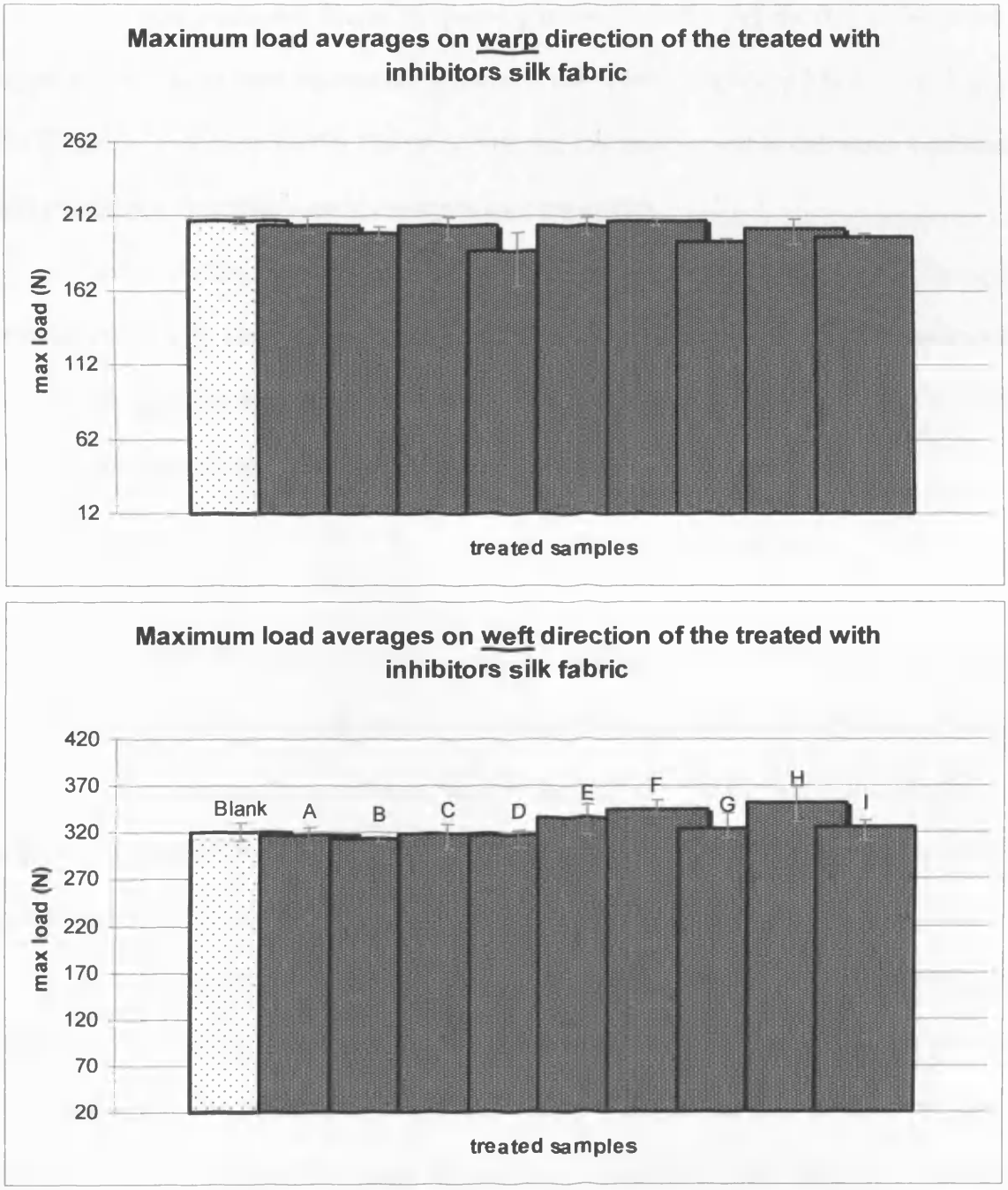


Figure 31.Breaking strength of treated with inhibitors and inhibitor combinations silk fabric on the warp and weft direction of the weave in comparison to the non treated sample. The error bars show the range of measurements either side of a mean of five replicate samples.

The improvement of breaking strength on either side of the weave direction (weft or warp) is also important depending on the specific object and it plays a role in the selection of display methods. Examples of this are the hanging tapestries which are usually hung along the weft direction of the weave (Hallet and Howell, 2005, 912) and therefore in this case the breaking strength of the textile in the weft direction is considered more important.

The more impressive results are given by inhibitor H in the weft direction of the weave, where it seems to increase the breaking strength of the treated samples by 9,62%. According to the Student's *t*-test performed for this set of samples, this improvement is statistically significant with *t=-3,84* and *P=0,0049,* even at the significance level of 1%.

On the contrary, inhibitor D shows a negative change in the breaking strength in the warp direction of -10,10%. However, with *t=3,20* and *P=0,013*, the Student's *t*-test at 1% significance level shows that samples treated with inhibitor D do not differ significantly in breaking strength from the non treated ones.

Changes in Elongation

Changes are also found in the elongation at rupture. These changes can be seen in Table 26, on the warp and weft direction of the fabric as well as the overall change in both directions. A minus (-) in the column showing the % changes, indicates a loss in elongation, while a plus (+) indicates a gain in elongation. The elongation of the treated samples, expressed by the arithmetic mean of percent elongation at rupture, is given in the form of graph in Figure 32.

It is obvious that elongation is strongly affected by treatment with photodegradation inhibitors. It was already observed by macroscopic investigation of the treated samples, that silk fabric became stiffer after application of the additives and changes in flexibility were also observed by hand examinations. These observations are reflected in the changes in elongation shown in this test. Only one inhibitor combination (F) gives a positive result in change of elongation (+3,61%) while all the rest give negative numbers. This change observed in inhibitor F

treatments is however considered not statistically significant giving in the *t*-test at 1%significance level, *t=-2,19* and *P=0,060.*

Table 26. Per cent elongation averages of silks treated with inhibitor and per cent change in elongation, in comparison to the non treated sample

	WARP			WEFT			
Treated samples	**elong%**	**St. Dev**	**% change**	**elong%**	**St.Dev**	**% change**	**Overall %change in elongation**
BLANK	18,42	0,61		12,83	0,28		
Inhibitor A	17,56	0,70	**-4,65**	12,52	0,52	**-2,43**	**-3,73**
Inhibitor B	16,93	1,51	**-8,09**	11,53	0,16	**-10,15**	**-8,93**
Inhibitor C	17,26	1,08	**-6,27**	11,94	0,41	**-6,93**	**-6,54**
Inhibitor D	14,75	2,19	**-19,93**	11,45	0,65	**-10,78**	**-16,17**
Inhibitor E	17,06	1,82	**-7,40**	13,86	0,48	**+7,96**	**-1,09**
Inhibitor F	18,73	0,16	**+1,69**	13,65	0,82	**+6,37**	**+3,61**
Inhibitor G	16,57	0,60	**-10,05**	11,86	0,95	**-7,62**	**-9,05**
Inhibitor H	15,51	1,12	**-15,80**	14,08	1,43	**+9,73**	**-5,31**
Inhibitor I	17,62	0,26	**-4,34**	12,50	1,15	**-2,61**	**-3,63**

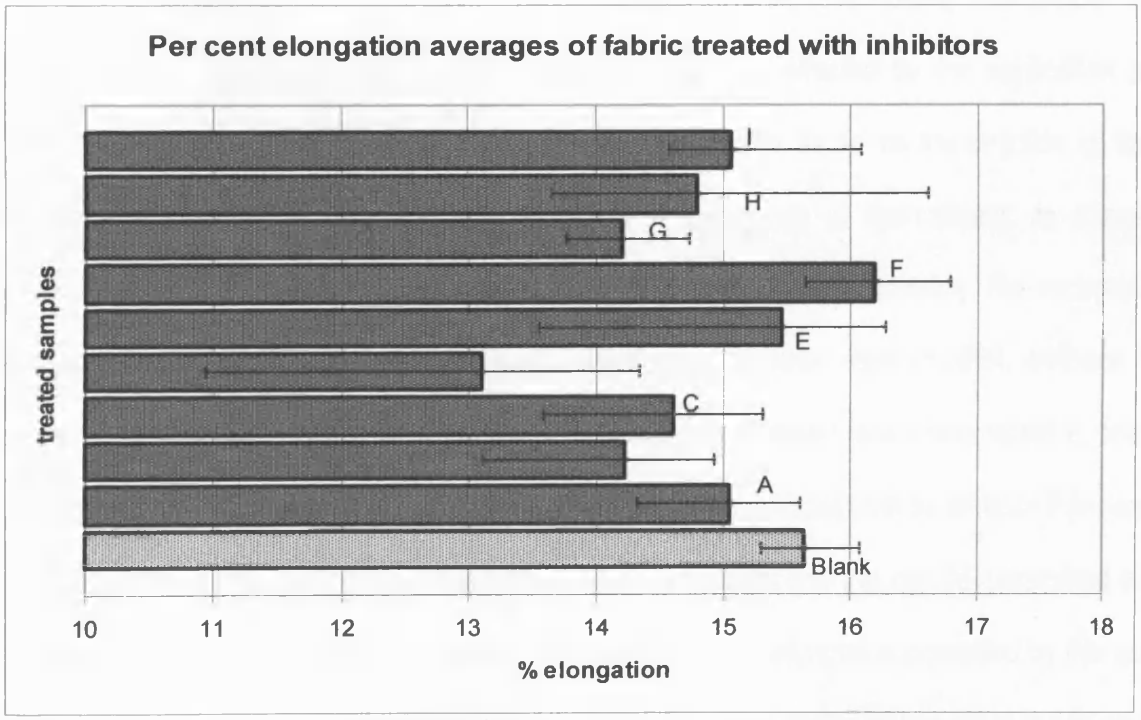


Figure 32.Overall change in % elongation of the treated with inhibitors and inhibitor combinations silk fabric in comparison to the non treated sample.

A negative change on elongation means reduction in flexibility, an important property of silk. Historic silks with reduced flexibility are more sensitive on handling and especially during folding for storage or display purposes. A reduction in flexibility usually means a change in the appearance of the object, for example in the case of light weight silk costumes with pleats which look stiffer and inflexible. When elongation is negatively affected historic textiles may deform or even collapse during handling for conservation, storage, transportation or display.

The worst results are attributed to inhibitor D which causes the highest negative change in elongation of the treated fabric (-16,17%) which is considered a significant negative result. The Student's *t*-test done for this set of samples showed that at significance level of 1%, this negative change in elongation is statistically significant with *t=4,14* and *P=0,0033.* The changes caused by the same additive in breaking strength are also the worst among all selected inhibitors and therefore the overall changes in mechanical properties of the fibres treated with additive D (hindered amine antioxidant) is considered a major disadvantage of the additive.

The results also vary according to the weave direction. It is noticed with almost all treatments that the warp direction of the fabric is negatively affected by the application of inhibitors. In this case too the changes in elongation properties as far as the direction of the weave is concerned are also important according to the needs of each object, its shape, construction pattern and forces to be induced during display and general handling. The exception is again inhibitor combination F, which has a surprisingly positive result (1,69%). Inhibitor F consists of the benzophenone absorber A and the polymeric hindered amine antioxidant E, both of which are giving negative results, of low percentage though. As a conclusion, inhibitor F proves to be beneficial to the mechanical properties of the treated fibres and this can be considered an advantage of the specific additive. However, this improvement in elongation presented by this set of samples is not statistically significant according to the *t*-test, giving values of *t=-0,156* and *P=0,88* at 1% level of significance.

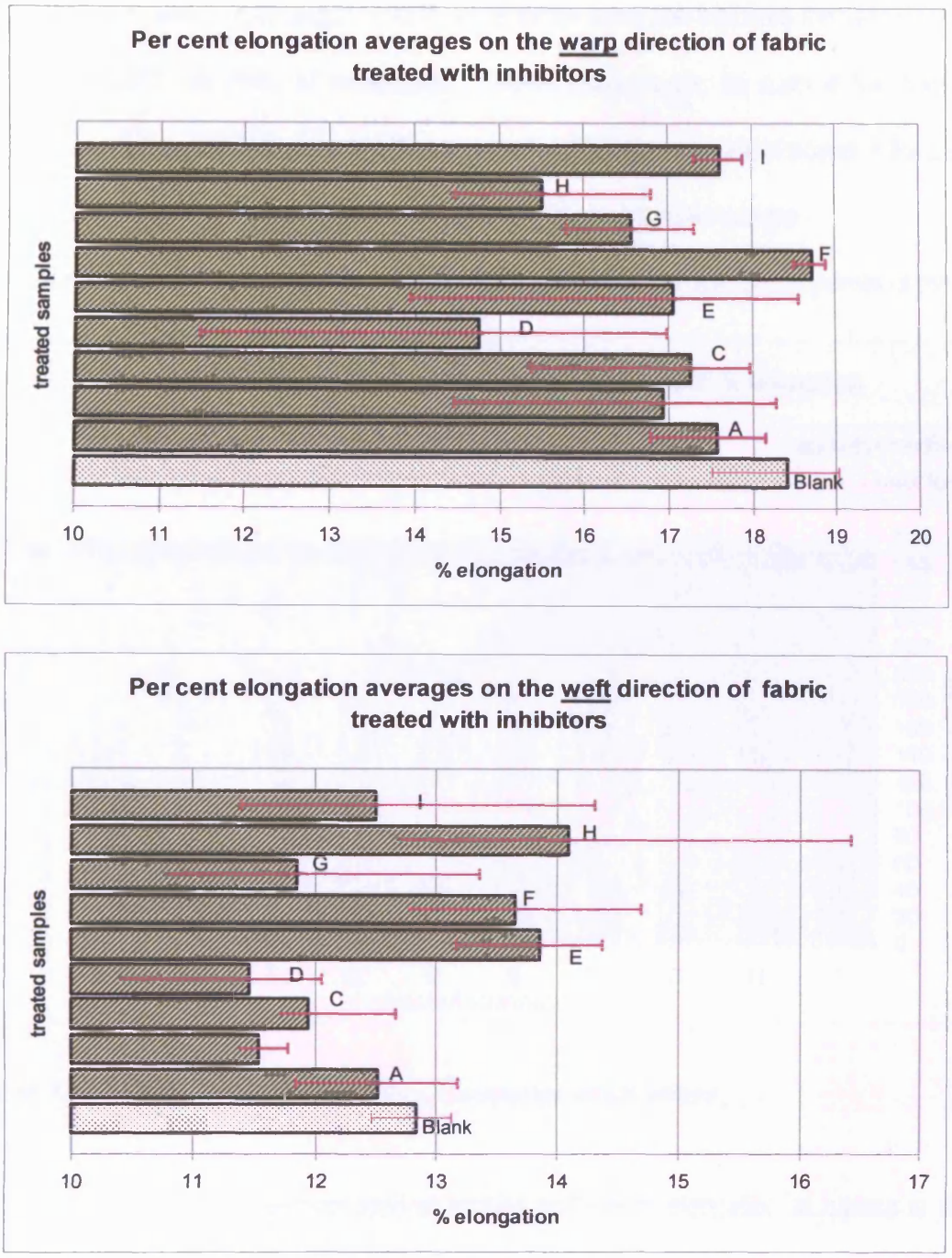


Figure 33. % elongation of the fabric in comparison to the non treated sample. Error bars show the range of measurements either side of a mean of five replicate samples.

On the other hand, only three out of nine inhibitor treatments proved to be beneficial to the elongation property in the weft direction of the weave. The three treatments showing an improvement in the weft direction are inhibitors E, F and H. However, from these three treatments only the one with inhibitor E can be considered significant following the *t*-test results, at 1%

significance level, with *t=-4,02* and *P=0,0038*, while for the other two inhibitors the same test gave values of *P=0,070* and *P=0,097* respectively. These changes can be seen in the graphs of Figure 33 where the arithmetic mean of % elongation in the warp and weft direction of the treated with inhibitors silk fabric, is presented in comparison to the non treated sample.

Figure 34 summarises the overall effects of the inhibitors on the mechanical properties of the silk.

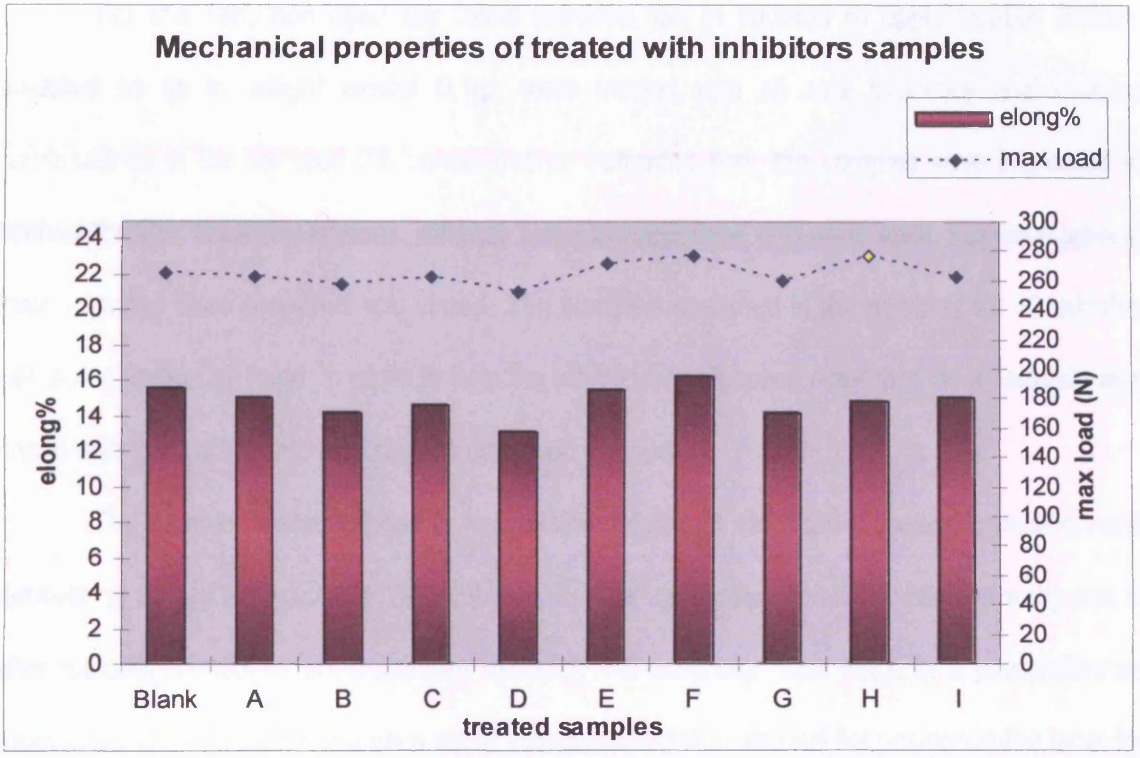


Figure 34. Tensile strength and elongation averages of samples treated with inhibitor

In this graph the maximum load at rupture and the % elongation at rupture is shown together for ease of comparison. It is apparent that the changes observed in tensile strength and elongation of the samples after treatment are more or less proportional. This means that if a treatment reduces the breaking strength of the fabric, its elongation will also be negatively affected. The only exception is the treatment with inhibitor combination H which reduces the elongation of the treated fabric on the one hand, but nonetheless increases its breaking strength more than any other additive. Inhibitor H is a combination of the benzotriazole absorber C and the polymeric hindered amine antioxidant E, neither of which present similar results.

9.4 Testing for removability

In order for a material to be considered as a conservation treatment its removability must be evaluated. In order to evaluate if the applied photodegardation inhibitors can be removed from the silk fabric, simple dry cleaning methods were applied. The newly introduced materials should be soluble in the same solvent used for their application.

For this test, non dyed silk fabric samples, cut in squares of approximately 5x5cm, adjusted so as to weight almost 0,1gr, were treated with all nine inhibitors and inhibitor combinations in the selected 2% concentration. Following that, the samples were immersed in each of the four solvents: acetone, ethanol, tetrachloroethylene and white spirit. For each solvent three samples were prepared and tested. The samples remained in the solvents for 10 minutes with soft agitation by hand, in order to help the inhibitors to dissolve. After that, every sample was rinsed with fresh solvent to remove any dissolved residue.

The samples were weighed to four decimal places in the three stages of application and removal: a) before application of the inhibitors, b) after application when samples were dry and c) after removal procedure when samples were dry. All weighings took place in a preconditioned room at 20°C and 35%RH and each set of samples was left in relaxed flat position in the room for at least 24hours between treatment, removal and weighing. These detailed weighings indicate the amount of inhibitor remaining in the sample.

Furthermore, samples after cleaning (removal) were examined in the scanning electron microscope in comparison to the treated samples and differences in the external surface view of the fibres were distinguished.

9.4.a Evaluation of reversibility

The average % remnant of each inhibitor, and the standard deviation of the three measurements, are given in Table 27. Detailed weighings and relevant graphs were prepared and given in *Appendix B.5*

Table 27. Per cent remnant averages of inhibitors and inhibitor combinations on non dyed silk fabric after cleaning procedure, using different solvents.

inhibitor removed with tetrachloroethylene	**% remnant of the additive on fabric after cleaning**	**Standard deviation**
Inhibitor A	0,94	0,42
Inhibitor B	1,03	0,06
Inhibitor C	0,95	0,46
Inhibitor D	0,80	0,45
Inhibitor E	1,99	0,39
Inhibitor F	3,02	0,39
Inhibitor G	2,52	1,63
Inhibitor H	2,68	0,48
Inhibitor I	3,96	2,05
inhibitor removed with acetone		
Inhibitor A	0,70	0,26
Inhibitor B	1,04	0,15
Inhibitor D	1,24	0,14
Inhibitor E	1,33	0,06
Inhibitor F	1,23	0,07
Inhibitor G	1,15	0,30
inhibitor removed with ethanol		
Inhibitor A	0,93	0,31
Inhibitor B	1,70	0,47
Inhibitor D	1,22	0,38
Inhibitor G	0,83	0,13
inhibitor removed with white spirit		
Inhibitor B	0,92	0,11
Inhibitor C	0,87	0,33
Inhibitor D	2,30	1,97
Inhibitor I	1,02	0,05

It can be noticed that none of the additives can be completely removed from the silk fibres. The inhibitors and inhibitor combinations used in this study were of course soluble in the selected solvents selectively and all in tetrachoroethylene solvent after application on the fabric, but a trace of them remained in the fibres and this can be observed by the samples' weight.

The average residue of all applied inhibitors to the silk samples is 1,38% of dry weight which is considered a considerable amount in comparison to the average add-on (8,51%) when inhibitors where introduced into the fibres. On the other hand there are samples that showed an average remnant of inhibitors equal to 0,7% after removal and this is a promising result. Nevertheless, the preliminary assumption from this test is that none of the selected inhibitors can be totally removable.

An interesting observation among the different solvents used, is that every additive reacts differently as far as removability concerns with every solvent used for cleaning. This can be seen in detail in the graphs prepared and presented in *Appendix B5.5.* One of these graphs, showing the behavior of inhibitor B during removal using different solvents, is given below in Figure 35.

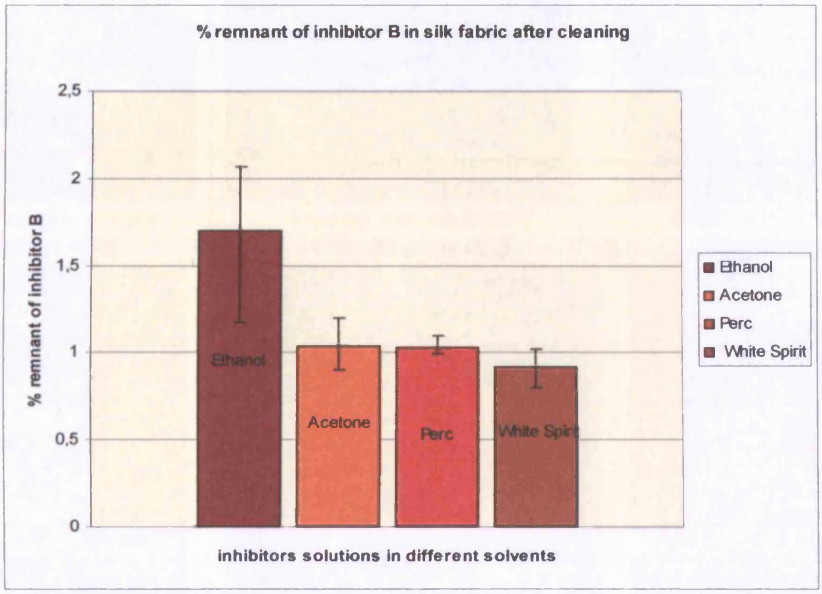


Figure 35. Residue percentage averages of inhibitor B on silk fabric after removal using different solvents

A surprising result is also presented in this test by the use of tetrachloroethylene as a solvent for removing photodegradation inhibitors from the silk fibres. Tetrachloroethylene shows to be rather poor at removing the inhibitors, even though it is the best solvent for them during the preparation of the solutions before application. There is therefore the possibility that the solubility of the additives is changed after dissolution and evaporation of the solvent.

The samples were also studied in the SEM so as to have comparative views before and after cleaning. The observations are based again on the external view of the fibres as it is not possible to identify the inhibitors absorbed in the inner parts of the fibre with this analytical technique.

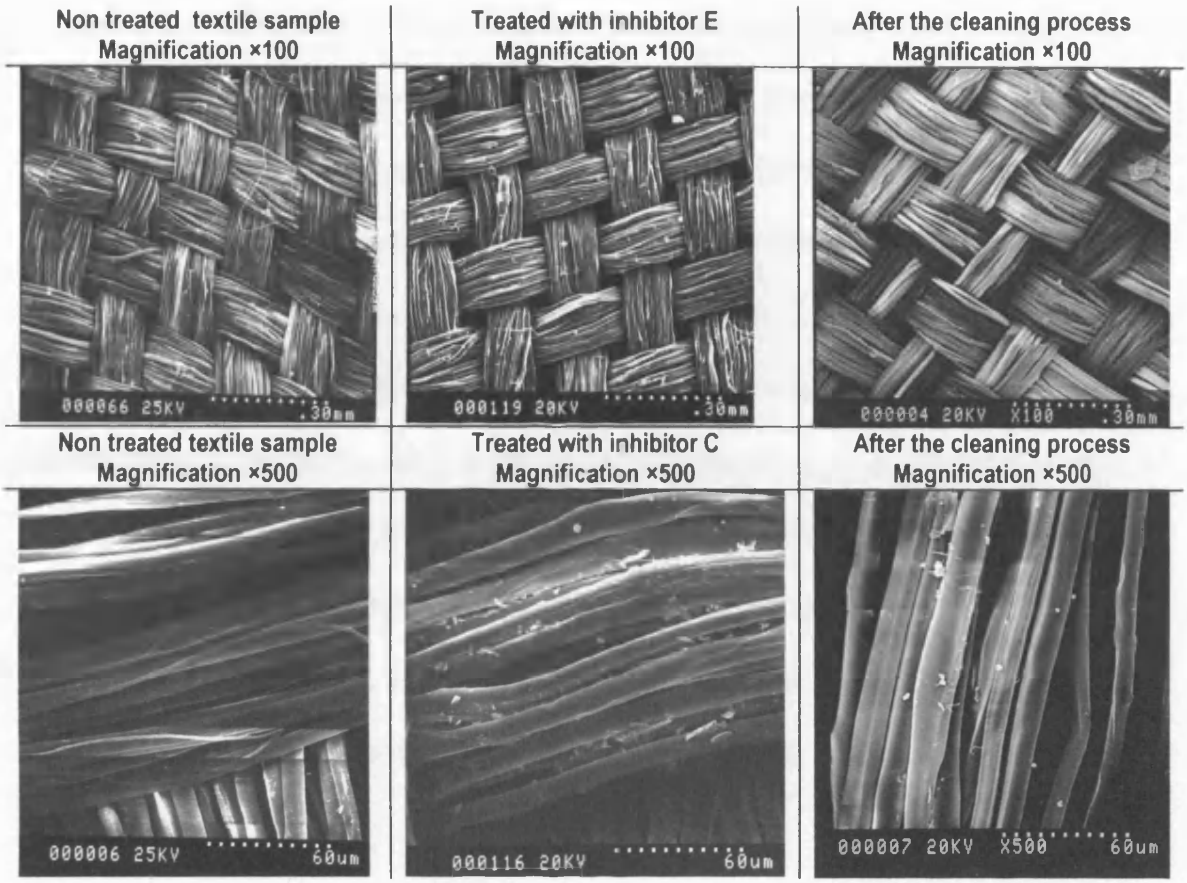


Figure 36. Comparative photographs: before treatment with inhibitors; after treatment; after removal of inhibitors

What was generally observed was that most of the excess amount of the additives observed previously (after the inhibitor application to the fibres) on the surface of the fibres in the form of separate particles, is now vanished. This means that, at least the quantity of inhibitors which was not absorbed by the fibres is dissolved in the solvent after the cleaning procedure. Some comparative photographs taken from the SEM are given in Figure 36. It can be noticed that in lower magnifications the external view of the fibres is very clean, almost in the same condition as presented before any application of the inhibitor, while in higher magnifications, traces of inhibitor particles can be traced in the fibre surface.

Section summary

Evaluation of treated with inhibitors samples showed that non dyed model samples became yellower after treatment and those dyed with natural red dyes show no noticeable colour change. Colourimetric measurements proved that there are some measurable colour changes on the treated samples and this is dependent on the dyestuff and the solvent used.

Microscopy investigations showed that inhibitor particles accumulated in the fibre surface and their shape and form is different for every additive. Mechanical properties of the treated fibres are not changing significantly after treatment although there are some noticeable changes on elongation, in relation to the direction of the weave, as the silk fabric became slightly stiffer.

Evaluation of removability of the additives showed that none of the selected inhibitors can be completely removed form the fabric, but all of the additives remain soluble in a range of solvents to considerable degree dependent on the solvent.

10. Exposure to light, results and evaluation

After treatment with different photodegradation inhibitors, all the dyed samples were exposed to electromagnetic radiation in order to evaluate the effect of the inhibitors in improving light fastness. As exposure in direct sunlight is a long term procedure and always affected by external factors that would be very difficult to control and measure, the choice of an artificial light source working in a controlled manner was preferred. This artificial light source must imitate the sunlight, as it is known that there are many light sources that emit radiation of different wavelengths than those of the daylight reaching the earth. As mentioned before the electromagnetic radiation reaching the earth's surface has wavelengths no shorter than 290nm; when this passes through an ordinary window glass, radiation above 315nm passes through (Feller, 1994). Therefore, in the case of museum environmental tests, all light sources emitting radiation below 315nm are inappropriate for light fastness testing.

The equipment as well as the experimental plan chosen for artificial light testing in this research was designed according to the aims and objectives of this study. The choice and design were also dependent on the availability of the equipment, the total cost and the allowed time of use.

In summary, four light fastness tests were performed in the order presented in this chapter, and each test (other than the first) was determined by the results and the primary evaluation of the preceding one. In the first three tests, dyed silk fabric samples were used, dyed with 7 natural red dyes and dye combinations and treated with 9 selected photodegradation inhibitors and inhibitor combinations. In the fourth and last test, as presented in *section 10.2.d* ,

only two representative series of dyed samples were tested, treated with nine inhibitors and inhibitor combinations.

The first test was based on the standard method BS 1006 :1990, UK-TN. "Colour fastness to artificial light: mercury vapour fading lamp test" and method 2 (6.2.3). This method was specially designed for quality control of all types of textiles and leather (BS 1006, 1990, UK-TN/1). In this first test the performance of the inhibitors on dyed silks was evaluated under a standard procedure.

The second was designed in such a way so as to keep time records of the exposure of the samples to electromagnetic radiation. In this case the samples were gradually covered in regular intervals of time and their colour changes were recorded. By this second test the fading rate of the dyes and the effect of the inhibitors were recorded.

In the third test, the effect of high temperature on the photodegradation procedure was evaluated. The samples were exposed to intense light in combination with high temperatures like those observed in sealed and non ventilated display cases in the summer time. This test can be considered as preliminary to the next, when the action of photodegradation inhibitors in constant and extreme environment was evaluated.

Finally in the fourth test, the selected samples were exposed in artificial light under predefined and controlled environmental conditions, so that the effect of relative humidity on the inhibitors could be evaluated.

10.1 The equipment used

Two light fading units were used. The first three tests were performed in a light fastness tester at the Institute of Archaeology research laboratory; several adjustments were made for the needs of this research. The fourth test was performed in an Atlas Xenotest Alpha+ unit under the services of the Clothing Textile and Fibre Technology Development Company (CLOTEFI)[28] based in Athens, Greece.

10.1.a The light fastness tester unit

In the three first tests the equipment used was a Microscal unit, LFT 1E-500 with a 500Watt MBTL air cooled lamp. The apparatus consists of a cylindrical metallic drum with its axis mounted vertically. At the centre of the drum the chosen light source was adjusted *(see Figure 37).*

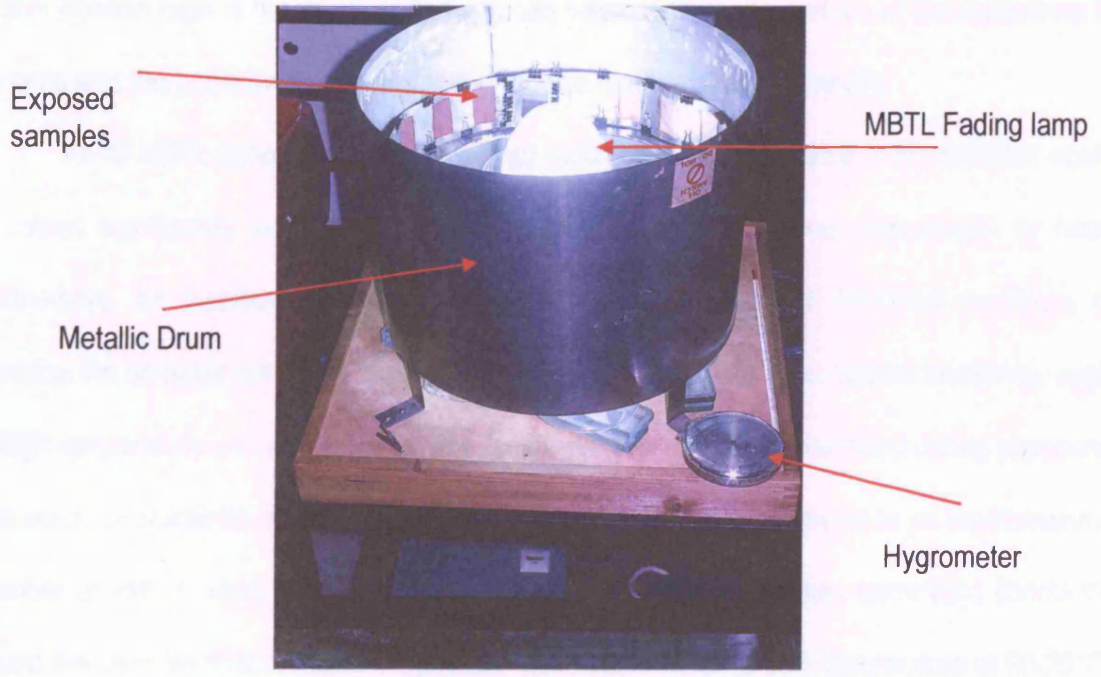


Figure 37. The apparatus as it was set up for the experimental procedure

One of the most widely used lamps in the colour fastness testing of materials is the so-called mercury-incandescent (MBFT) lamp. These lamps have been proved by several researchers to

[28] More information on CLOTEFI company at its website: www.etakei.gr

"give results in excellent agreement with those obtained in exposure to daylight" (Feller 1994, Giles *et al*, 1969, Park and Smith 1974 , Park 1976).

There are different types of mercury lamps and they are used according to the material to be tested and exposed. In the case of dyed textiles, which are the most sensitive to electromagnetic radiation, the MBTL type should be used, where light fastness above 5 (on the blue wool standards) is not encountered. The artificial ageing with light source, on naturally dyed materials, will be accelerated in a controlled way. It is found that an MBTL lamp, 500Watt, can give a grade 4 on the Grey scale for the Blue Standard No7 in 408 hours of exposure, whereas sunlight needs 1,400 hours to do the same (Park 1976). The UV content in this Microscal unit was approximately 600μW.lumen^{-1} and the average luminance at the sample surface was 24000lux.

Specimen masks were prepared with aluminium in such way so as to hold samples in vertical position around the drum. In this way the distance from the surface of the specimens to the lamp was the same for all samples and reference material *(see Figure 37)*.

As all MBTL lamps emit heat as well as radiation, the temperature of the samples would be raised significantly and there was a possibility to have additional degradation by heat. Furthermore, the humidity content of the fibres would be decreased. The ideal conditions of exposing the samples under electromagnetic radiation without any other factors interfering, such as high temperature and very low humidity, is to have a controlled environment during exposure. This would be achieved by special equipment either by putting the samples in an environmental chamber or use of water cooled light fastness testers. In the latter case, water runs constantly around the samples that are fitted in specially made casts keeping their temperature at 20-25°C. At the same time, small containers on the bottom of each sample are filled with solutions in order to control humidity to an average acceptable level of 45-50%RH. On the other hand, it is known that an increase of relative humidity during exposure often accelerates photodegradation. If required, high humidity can be achieved with the use of salt solutions, in order to accelerate the test.

10.1.b The Xenotest Apha+ unit

For the fourth light fastness test in this study a more sophisticated unit was used which satisfies all the above mentioned requirements. The Atlas Xenotest Alpha+ unit is a weathering instrument for testing the light fastness and weatherability of textile materials under specified environmental conditions.

The unit is composed of a closed environmental chamber in the centre of which an air-cooled xenon lamp with adjustable power range is placed. Around the lamp, specially designed sample holders are arranged at equal distances. A mechanism is used for slow rotation of the sample holders around the lamp, so that all specimens have the same light exposure during the test. Inside the chamber, temperature and relative humidity can be adjusted in a predefined range and their values during the test are recorded electronically. The selected relative humidity levels are achieved with the use of an ultrasonic humidification system.

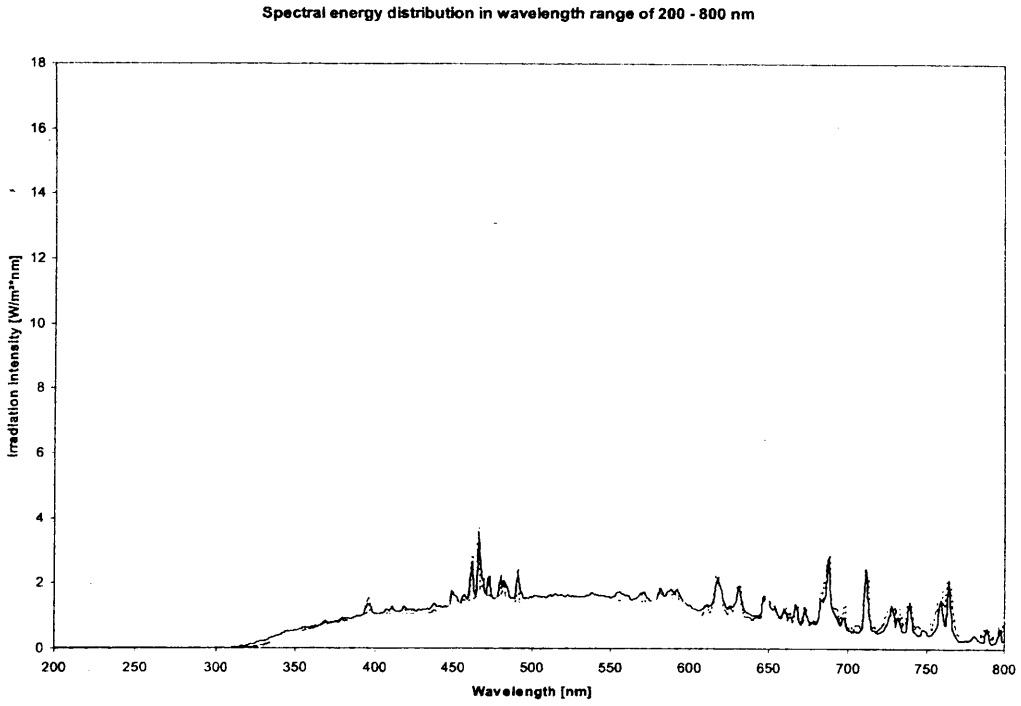


Figure 38.Spectral energy distribution of the xenon arc lamp used in the experiment *

*data taken from specifications manual of the equipment

The lamp used for this experiment was a xenon lamp NXE 200HE, 7 filters IR as specified by the standard testing method ISO 105-B02:1994. In this case the lamp had a wattage of 2000W and it is surrounded by a filter system consisting of a quartz inner cylinder, an additional lamp-chimney of seven heat filters and an outer cylinder of ultraviolet filter glass in order to achieve the required wavelength distribution imitating the sunlight through an ordinary window glass *(see Figure 38)*. The space between the xenon arc lamp and the filtering device is cooled by a current of air which is discharged into the open atmosphere. The irradiance given by the lamp was 42W/m^2.

10.2 Experimental planning

10.2.a Light fastness test No1 (BS 1006:1990)

For this test silk fabric samples were cut into square pieces of 6x6cm regardless of the direction of the weave and treated with nine inhibitors and inhibitor combinations as described before.

Samples were adjusted to the specially made aluminium casts in such way as to expose half of the sample (3x6cm exposure area) where the other half is covered by the aluminium foil *(see Figure 39)*. In this way, the colour difference will be easily distinguished during and after the exposure times. Twenty samples can be exposed each time together with the blue wool standards. This number includes samples dyed with two different dyes and treated with nine inhibitors (and inhibitor combinations).

A thermohygrograph recorded the environmental conditions during exposure in weekly cycles, placed close to the equipment. The system was air-cooled at all times with the operation of a fan and it was operated in a small closed laboratory room with no other use. Environmental data recorded by the equipment show a fluctuation in temperature between 25-30°C and relative humidity between 30-50%RH.

The colour differences produced in the samples were recorded every day in comparison to the grey scale and the reference blue wool standards. The samples were exposed until the

most resistant sample had reached Grey scale grade 3, following the (6.2.3.4) method of the BS 1006: 1990.

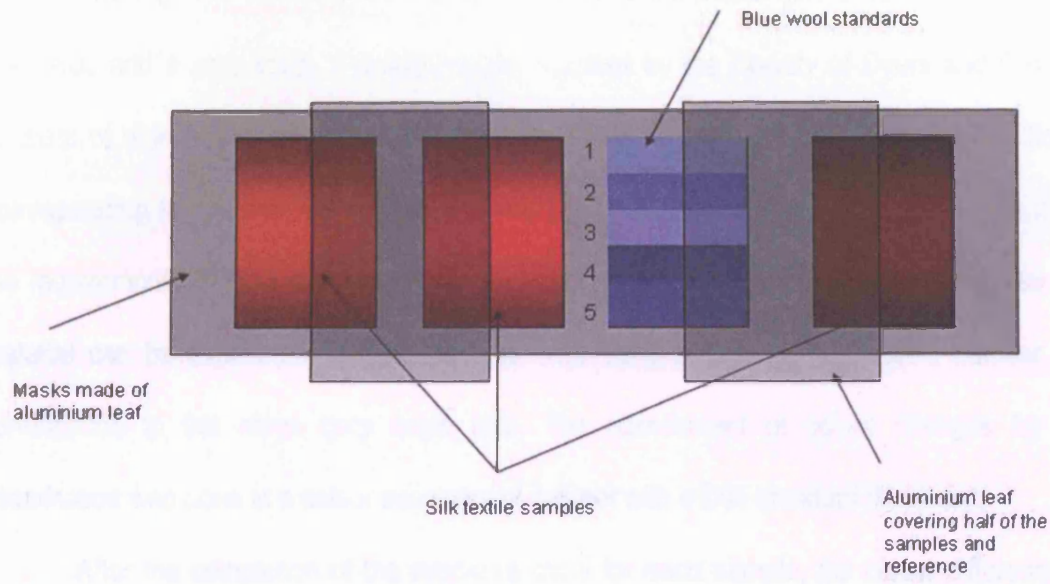


Figure 39. Graphic representation of the aluminium masks prepared for exposure of the samples

In this test the light fastness of the samples were evaluated in comparison to the *"Blue Wool Standards"* and a grey scale for assessing change in colour. The Blue Wool Standards are pieces of wool textile dyed with specific synthetic dyes with standard light fastness. The eight synthetic dyes used can be seen in the Table 28 and they are identified by the numerical designation 1 to 8.

Table 28. Dyes for blue wool standards 1 to 8 (BS1006:1990)

1	C.I. acid blue 104
2	C.I. acid blue 109
3	C.I. acid blue 83
4	C.I. acid blue 121
5	C.I. acid blue 47
6	C.I. acid blue 23
7	C.I. solubilized vat blue 5
8	C.I. solubilized vat blue 8

They extend from 1 (very low light fastness) to 8 (very high light fastness) in a way that each higher numbered standard is almost twice as fast as the former one (BS 1006 : 1990).

The exposed sampling material is compared to the colour difference of these blue wool standards and a grey scale. The grey scale, supplied by the Society of Dyers and Colourists, consists of nine pairs of non-glossy grey chips which illustrate the perceived colour difference corresponding to fastness rating 5, 4, 3, 2 and 1 with intermediate half steps in accordance with the requirements of ISO 105 (BS 1006): A02/A03. In this way, the final colour fastness of the material can be expressed in light fastness units according to the standard's number which corresponds to the same grey scale rate. The assessment of colour changes by visual examination was done in a colour assessment cabinet with a D65 standard illuminant.

After the completion of the exposure cycle for each sample, the colour differences are measured and each treated sample is given its light fastness grade, according to the blue wool references. This grade is finally compared with the light fastness grade of the non-treated sample in order to evaluate the ability of inhibitors to improve the light fastness of the dyed silks *(see section 10.4.a).*

10.2.b Light fastness test No2 (gradually covered samples)

For this test silk fabric samples were cut into square pieces of 6x6cm regardless of the direction of the weave and treated with nine inhibitors and inhibitor combinations as described before.

Samples were adjusted to the specially made aluminium casts in such way as to expose about 1cm of the sample where all the rest was covered. In this case a mobile aluminum cover was covering the rest of the sample, and this was moved, accordingly to the agreed time interval, for another 1cm every time *(see Figure 40).* The exposure intervals for each 1cm of the samples were 50, 100, 200,300 and 450 hours of exposure time. In this case each 6x6cm silk sample was divided into 6 zones for each exposure time and for the non exposed area. Twenty samples can be exposed each time. This number includes samples dyed with two different dyes and treated with nine inhibitors.

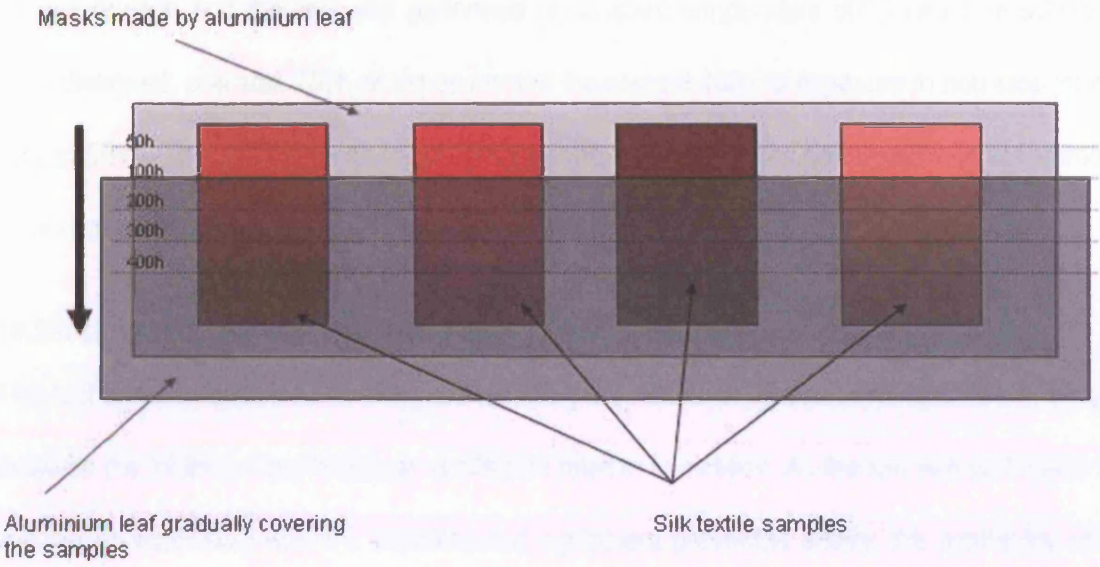


Figure 40. Graphic representation of the aluminium masks and cover prepared for the exposure of the samples for light fastness test No2

Again, a thermohygrograph recorded the environmental conditions during exposure in weekly cycles, placed close to the equipment. The system was air-cooled at all times with the operation of a fan and it was operated in a small closed laboratory room with no other use. The samples were allowed to have regular intervals of darkness, every twenty four hours, in order to regain their moisture content. Environmental data recorded by the equipment showed a fluctuation in temperature between 25-30°C and relative humidity between 30-40%RH.

The evaluation of colour changes after exposure was performed with colourimetric measurements *(see section 10.4.b).*

10.2.c Light fastness test No3 (High temperature)

For this test silk fabric samples were cut into square pieces of 6x6cm regardless of the direction of the weave and treated with nine inhibitors and inhibitor combinations as described before.

Samples were adjusted to the specially made aluminium casts in such way as to expose half of the sample where the other half is covered by the foil (3x6cm exposure area) in exactly the same way as in the light fastness test no1. In this way, the colour difference will be easily distinguished during and after the exposure times. The whole apparatus was inserted in a

laboratory oven and the test was performed at constant temperature 50ºC.Two time schedules were designed, one was 250h of exposure and the second 400h of exposure in non stop intense light at 50ºC. The evaluation of colour changes after exposure was performed with colourimetric measurements *(see section 10.4.c).*

10.2.d Light fastness test No4 (controlled relative humidity)

This last test was decided and designed following the results of light fastness test No3, in order to evaluate the inhibitors' performance at different relative humidities. As the test was performed in a specialized laboratory with the sophisticated equipment presented above, the availability of the unit and the extremely high cost of its use led to the selective elimination of the samples tested.

For this last test only two series of dyed samples was chosen, brazilwood and cochineal dyed silks, treated with all nine inhibitors (and inhibitor combinations). This choice was based on previous experimental results showing that these two dyes can be considered representative.

It was first of all decided to exclude all dye combinations in order to minimize testing parameters such as the complexity detected when dye combinations were involved. Among the red natural dyes used in this research, madder, brazilwood, cochineal and safflower, most of them are of vegetable origin and one is an animal dye. The only animal dye chosen is cochineal and along with its high light fastness, already known but also detected through the first three light fastness tests, it was selected for further testing. Cochineal is also a widely used dyestuff in orthodox ecclesiastical vestments because of its bright scarlet colour, commonly displayed in Greek museums *(see section 1.3.d).* From the other vegetable red dyes used in this study, brazilwood was chosen because of its low light stability, which appears opposite to cochineal, and the interesting results given in light fastness test No3 (*see section 10.4.c*). Safflower, which is also a vegetable and very light sensitive dyestuff, was excluded because of its negative results in all other three tests. Also safflower was introduced into the silk textile without a mordant and this places this dyestuff in a completely different group from the others. Finally, madder is a very common red dyestuff, very light stable and it showed a good performance with almost all

treatments in the three first tests. On the other hand, when used on silk and with alum mordant (as done in this study) it gives a dull light orange colour which shows no noticeable colour changes by eye examination during light fading tests. Therefore its participation in the fourth light fastness test was excluded.

According to the experimental plan set for this test, silk fabric samples dyed with brazilwood and cochineal and treated with nine inhibitors and inhibitor combinations were exposed in three cycles, keeping temperature stable and changing relative humidity levels. Control samples, without inhibitor, were also exposed. Using the environmental chamber of the available equipment, the chosen environmental parameters for each cycle could be stable during the exposure time, only if these choices complied with the equipment specifications *(see Figure 41).*

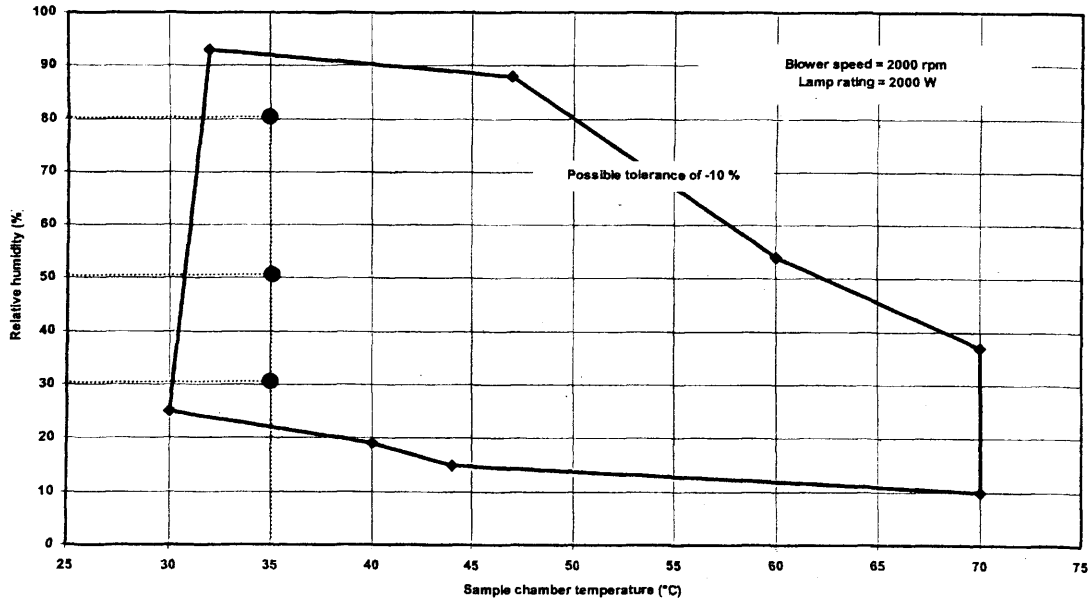


Figure 41.Humidity adjustment range given by the equipment specifications[29]. Levels of temperature and humidity inside the given area can be achieved by the unit. The three chosen humidity levels, keeping temperature stable, are plotted on the graph.

According to the given adjustment range of temperature and humidity levels of the available equipment, the three cycles chosen are given below:

[29] Graph taken from the Xenotest Alpha+ operating instructions manual, p.59.

1. Exposure cycle A: constant temperature of **35°C** and relative humidity **30%RH ±2** for 100hours.
2. Exposure cycle B: constant temperature of **35°C** and relative humidity **50%RH ±2** for 100hours.
3. Exposure cycle C: constant temperature of **35°C** and relative humidity **80%RH ±2** for 100hours.

For the needs of this test, samples were cut in dimensions 4.4x3.3cm to fit to the equipment specimen holders. Four samples could be placed in each holder (4.4X2.7cm exposed area). The samples were placed around the lamp along with the blue wool standards and rotated as shown in *Figure 42*.

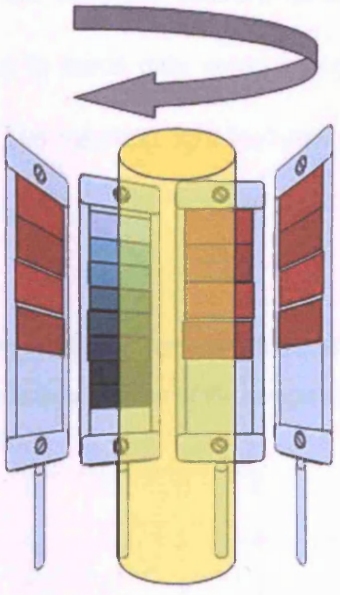


Figure 42. Graphic representation of the sample holder as placed in the chamber around the lamp

The assessment of colour change was done in comparison to the blue wool standards by visual examination in a colour assessment cabinet with a D65 standard illuminant, and with colourimetric measurements.

10.3 Light fastness evaluation

10.3.a Assessment of light fastness according to test No1 (BS 1006:1990)

In this test, the changes of each sample are compared with the changes of the blue wool references according to a grey scale.

The exposure to light was terminated for each set of samples when a contrast equal to grey scale 3 had been produced on the most resistant sample. The light fastness grade for each sample is the number of the blue wool reference which shows similar changes in colour and this is assessed by the visual contrast between exposed and unexposed parts of the same sample. If a sample showed changes in colour which were nearer to a reference midway between two consecutive references an intermediate rating was given, such as 2-3 for example (BS 1006:1990, UK-TN/5). The times of exposure are therefore different for every set of samples as the more lightfast dyes will need more time to reach grey scale 3 (e.g madder, 1439 h) than the more sensitive one (safflower, 130 h). The resulting light fastness grades are given in Table 29 and their gradation can be seen in *Figure 43*.

Table 29. Light fastness grades after exposure according to the method BS 1006:1990

Dyes		**Light fastness grades of the samples treated with photodegradation inhibitors**								
	Blank	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
Madder	5	6	6	6	5	6	6	5	6	6
Brazilwood	2	3	3-4	3	3	3	3-4	3-4	4	3-4
Safflower	2	2	2-3	2-3	2	2-3	3	2-3	2-3	2
Cochineal	4	6	6	6	5	6	5	5	6	6
Combination 1	3-4	4	5	5	5	5	4	5	6	3
Combination 2	3-4	3-4	4	4	4	4	3-4	4	4-5	3
Combination 3	5	5	6	5	6	6	6	6	6	6

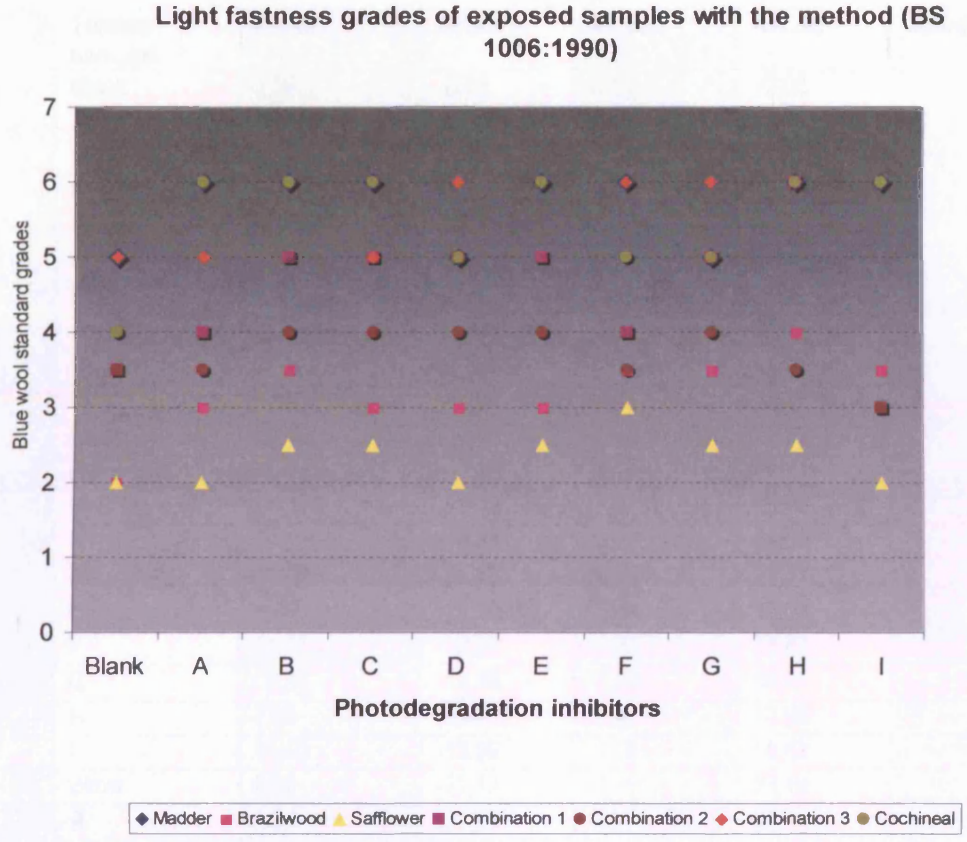


Figure 43. Chart representing the light fastness grades of the treated with inhibitor samples according to the blue wool standards and grey scale comparisons.

After the end of each exposure cycle, three colourimetric measurements were taken from the exposed and unexposed areas of the samples. The colour change evaluation was performed by colourimetric measurements with the use of a Minolta CR-221 chromameter with light source C, a 3mm diameter measuring area, and a 45° illumination angle. The meter was calibrated before each measuring session using a standard white plate. The results are summarized in Table 30 (all measurements are presented in *Appendix C.1)*

Table 30. Average colourimetric measurements of the samples for test No1

	Treated samples	Av. ΔL*	Av.Δα*	Av. Δb*	Av. ΔE	Standard Deviation of ΔE
Madder	Blank	9,29	-6,46	-4,06	12,02	1,0
	A	4,10	-2,05	-3,44	5,73	3,1
	B	6,23	-3,68	-2,80	7,76	0,8
	C	6,15	-2,91	-2,20	7,15	1,6
	D	3,91	-1,41	-1,62	4,46	1,4
	E	6,21	-2,64	-1,70	6,96	0,4
	F	6,01	-2,78	-2,29	7,00	1,1
	G	7,29	-4,48	-2,90	9,04	0,4
	H	7,69	-4,43	-2,71	9,28	2,4
	I	3,08	-1,06	-1,83	3,74	1,6
Brazilwood	Blank	11,44	-13,50	-0,85	17,72	0,7
	A	10,28	-11,23	-2,37	15,41	0,9
	B	8,75	-10,37	-2,41	13,78	0,6
	C	10,75	-14,24	-2,97	18,09	1,0
	D	11,77	-14,48	-2,01	18,77	1,1
	E	9,76	-11,38	-0,73	15,01	2,1
	F	11,07	-10,97	-1,23	15,63	0,2
	G	11,30	-12,39	-1,23	16,81	0,3
	H	7,30	-9,68	-2,41	12,36	0,5
	I	11,45	-12,25	-1,19	16,82	0,3
Safflower	Blank	9,05	-21,19	-2,59	23,19	2,5
	A	8,94	-21,25	-4,27	23,44	2,0
	B	9,17	-21,93	-2,64	23,92	0,6
	C	7,92	-19,33	-3,44	21,17	1,0
	D	9,04	-20,73	-4,12	22,99	2,2
	E	9,89	-23,07	-4,70	25,54	0,4
	F	9,28	-21,20	-1,91	23,22	1,0
	G	10,39	-24,26	-4,22	26,73	0,1
	H	8,86	-25,16	-1,65	26,73	4,2
	I	11,15	-26,93	-1,92	29,21	2,3
Cochineal	Blank	7,09	-1,15	-1,50	7,33	0,5
	A	4,92	-1,50	-1,00	5,24	0,4
	B	6,40	-0,63	-0,96	6,51	0,6
	C	4,91	-2,54	-1,65	5,77	0,1
	D	7,20	-1,29	-1,26	7,42	0,7
	E	5,19	-1,17	-0,32	5,33	1,0
	F	6,18	-5,09	-1,97	8,24	1,5
	G	6,14	-2,18	-1,70	6,74	1,5
	H	5,94	-1,41	-1,17	6,22	0,6
	I	5,40	-4,71	-2,34	7,54	0,4
Combination 1	Blank	5,31	-1,36	-0,67	5,52	1,2
	A	3,13	-2,17	-1,86	4,24	0,4
	B	4,15	-4,47	-0,36	6,11	1,3
	C	2,96	-3,76	-2,69	5,49	0,6
	D	8,47	-5,02	-1,66	9,99	1,5
	E	6,65	-0,79	-0,59	6,73	0,8
	F	5,65	-1,68	-0,38	5,91	1,0
	G	5,69	-1,73	-0,70	5,99	0,2
	H	4,31	-0,01	-0,52	4,34	0,8
	I	7	-2,21	-0,05	7,34	1,0

Combination 2	Blank	2,86	-0,75	-1,83	3,48	0,6
	A	5,11	-0,38	-1,35	5,30	0,5
	B	3,64	1,60	-0,78	4,05	0,5
	C	3,38	0,55	-1,54	3,76	0,8
	D	3,71	2,37	1,85	4,78	0,5
	E	5,20	0,67	-0,57	5,27	0,9
	F	4,05	0,27	1,06	4,19	0,7
	G	4,42	0,48	-0,45	4,47	0,1
	H	4,62	0,72	0,79	4,75	0,8
	I	4,02	0,93	-1,34	4,33	1,1
Combination 3	Blank	2,42	-4,65	1,39	5,42	0,1
	A	3,19	-4,84	0,51	5,81	0,3
	B	-1,03	0,43	1,40	1,79	3,3
	C	1,33	-1,66	0,33	2,15	1,1
	D	1,14	-4,16	1,37	4,53	0,3
	E	0,26	-4,75	1,38	4,95	0,1
	F	0,91	-3,60	0,20	3,72	0,3
	G	-0,42	-3,87	1,31	4,11	0,4
	H	0,58	-3,46	0,58	3,56	0,3
	I	1,18	-4,67	0,75	4,87	0,1

There are some promising results, as the light-fastness on some treated samples is increased to a very satisfactory level. One can easily observe that every dye reacted differently with every inhibitor. In the case of the madder samples, the results are very promising. All the inhibitors seem to prevent fading of the dye to a considerable degree. An increase of 63% can be achieved using inhibitor D, while A also showed a significant increase of 50%. In both cases the result is statistically significant according to the *t*-test performed at 5% significance level, with t=7,55 and p=0,0016 for inhibitor D and t=3,24 and p=0,032 for inhibitor A.

In the case of brazilwood, some increase in the light fastness is noticed after treatment with inhibitors A, B and E, with the maximum increase of 20% showed by B. This result is also considered significant giving t=7,70 and p=0,0015 in the *t*-test at 5% level of significance. Inhibitors C and D, on the other hand, appear to cause photosensitization rather than photoprotection, as they decrease the lightfastness by about 2-5%. However, neither of these results is statistically significant as *t*-test at 5% level of significance gave t=-0,465 and p=0,67 for inhibitor C and t=-1,34 and p=0,25 for inhibitor D. The most interesting additive seems to be inhibitor H, since it has improved the light fastness of brazilwood dyed silk about 40%. It is

interesting to notice that inhibitor H is a combination of an absorber and an antioxidant. This indicates synergism of the two inhibitors, working together for a better result than they can achieve alone. Furthermore the given result by inhibitor H is statistically significant according to the Student's *t*-test at 5% significance level with t=11,2 and p=0,0004.

In the case of the safflower samples, the results are more puzzling, as some additives proved to work as sensitizers to the dye, having as a result the samples to show greater colour difference when treated. In this case, additive C showed the better performance but it was not statistically significant, with t=1,27 and p=0,27 at 5% significance level. The fact that the safflower dye is applied to the fibres without any mordant is making it always very susceptible to photodegradation.

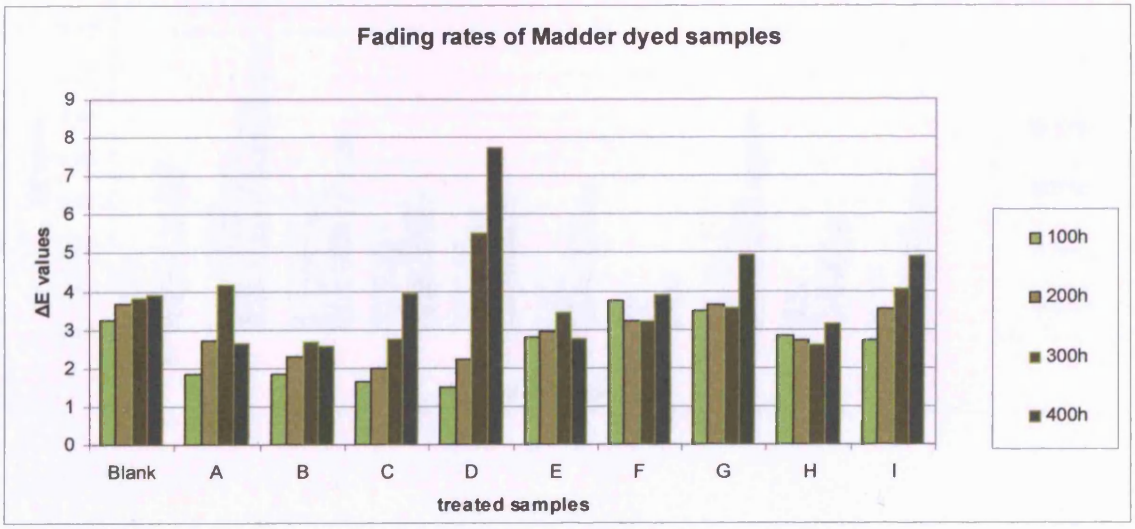
On the cochineal samples it can be noticed that inhibitors A, C , E and H provide a good protection against photodegradation increasing the light fastness by 28%, 21%, 27% and 16% respectively. According to the *t*-test at 5% level of statistical significance, in all the above mentioned cases except inhibitor H, the results are statistically significant with t=5,95 and p=0,0040 (inhibitor A), t=5,76 and p=0,0045 (inhibitor C), t=3,59 and p=0,023 (inhibitor E) and t=2,48 and p=0,068 (inhibitor H) respectively. An acceleration of fading was also noticed, in this case by inhibitor combination F, showing an increase of fading of 11%, but this is not considered statistically significant giving t=-0,586 and p=0,59 at 5% level.

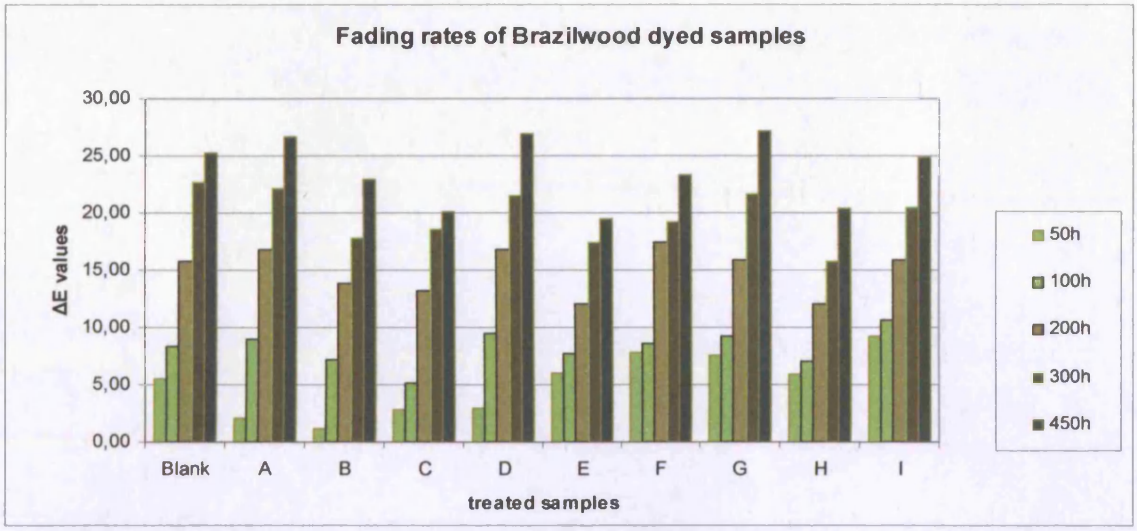
Samples with dye combinations are far more complicated than the ones dyed with single dyestuffs. Samples dyed with dye combination 1, brazilwood, madder and tannin, show less fading when treated with inhibitors A and H but there was an important acceleration of fading caused by additive D (44%). The result given by inhibitor D is statistically significant with t=-4,24 and p=0,013 at 5% significance level. On the other hand, samples dyed with combination 2, brazilwood, madder, tannin and lawson, seem to antagonize with all the inhibitors and inhibitor combinations tested, as their light fastness was decreased in all cases. Finally, samples dyed with combination 3, cochineal, brazilwood and tannin, showed a better performance when treated

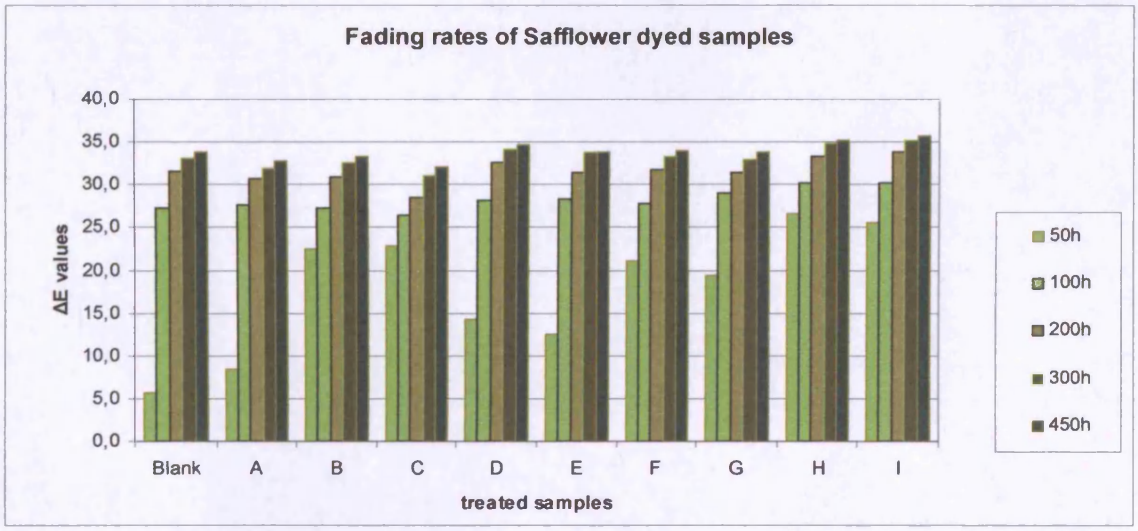
with inhibitors B and C as their light fastness was increased by 66% and 60% respectively, but also inhibitor combinations F and H seem to provide good protection to this set of samples. However, Student's *t*-test showed that the increase of lightfastness due to treatment with additives B and C is not statistically significant, with t=0,130 and p=0,90 and t=2,44 and p=0,071 respectively at 5% significance level. On the contrary, the positive results given by inhibitors F and H are statistically significant with t=9 and p=0,0008, and t=9,72 and p=0,0006 respectively.

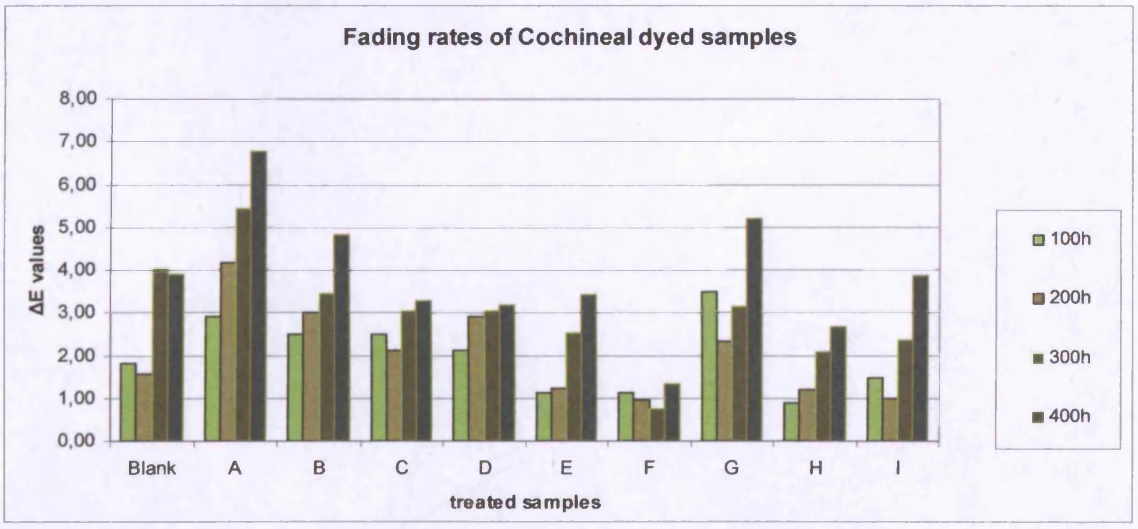
10.3.b Assessment of light fastness according to test No2 (gradually covered samples)

In this test the samples were gradually covered during predetermined periods of time in order to investigate fading *rates* and the changing of these rates due to the inhibitors. The fading rates are presented in the form of charts (presented in detail in *Appendix C.3*) and they are assessed by colourimetric measurements for each period of exposure in comparison to the non exposed part of the samples. Colourimetry was performed with the use of the Minolta CR-221 chromameter, using the same procedures as before. In each chart the fading rate of the non treated sample is given together with the rates of the treated samples of the same origin. In the charts in *Figure 44* , the overall performance of all additives is presented for each dye and dye combination samples, while in *Appendix C, section C2 and C.3* the fading rate of each treated sample with every inhibitor, in comparison to the non treated sample each time, is presented separately.




Fading rates of Brazilwood dyed samples
30,00
25,00
20,00
15,00
10,00
5,00
0,00
ΔE values
Blank
A
B
C
D
E
F
G
H
I
treated samples
50h
100h
200h
300h
450h


Fading rates of Safflower dyed samples
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
ΔE values
Blank
A
B
C
D
E
F
G
H
I
treated samples
50h
100h
200h
300h
450h


Fading rates of Cochineal dyed samples
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
Blank
A
B
C
D
E
F
G
H
I
treated samples
100h
200h
300h
400h

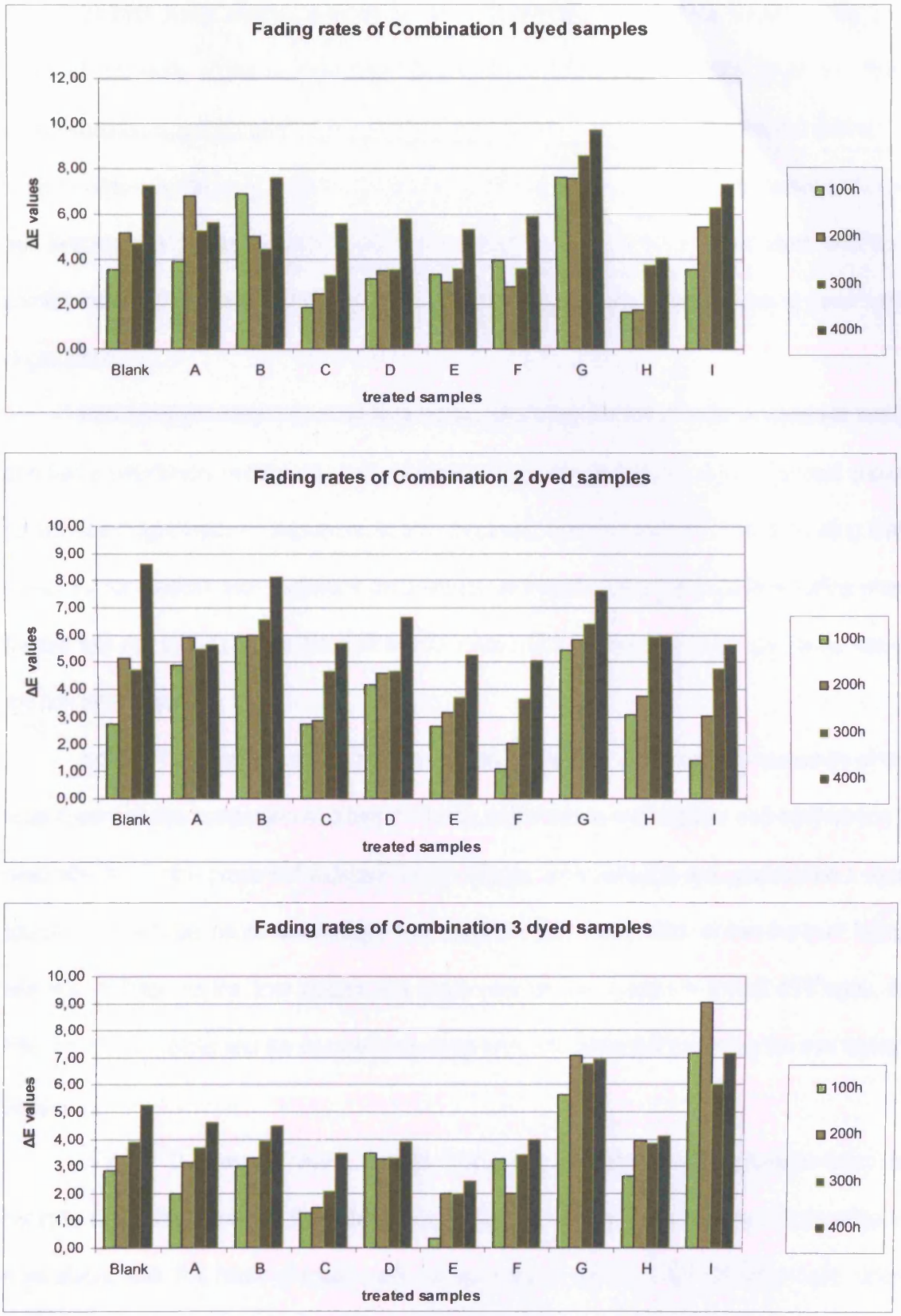


Figure 44. Fading rates of silk fabric samples dyed with different dyes and treated with inhibitors

Inhibitor A has a relatively good performance with madder dyed silk but only in the first hours of exposure; when the exposure time exceeds 300 hours its ability to protect from photodegradation is diminished. When applied to samples dyed with combination 3, it seems to work satisfactorily during all periods of time having the same curve as the non treated samples but keeping the colour difference level to a lower degree. With all other dyes and dye combinations the performance of inhibitor A is either poor or sometimes is causing faster light degradation.

Inhibitor B provided a good protection from photodegradation on madder dyed silk and it also had a satisfactory performance with brazilwood dyed silk, but all the other dyes have shown no significant light fastness improvement after treatment with this additive. It is interesting that, except for the madder and brazilwood dyed fabrics, all the rest exhibit more severe fading when treated with this inhibitor at the first 100 to 200 hours and after that they follow the fading rate of the non treated sample.

Inhibitor C has shown that is able to eliminate the colour difference after exposure of the most dyes and dye combinations. It had the better performance with madder and combination 3 dyed silks but it also presented reduced colour changes on brazilwood and combination 1 dyed samples. It has to be mentioned, though, that in madder dyed fabric which shows the least fading with this inhibitor, as the time passes and finally reaches the maximum limit of 400 hours, its effectiveness vanishes and the sample is showing the same colour difference as the non treated sample.

Inhibitor D does not seem to offer significant protection from photodegradation of naturally dyed silks except in the case of combination 1 dyed samples and its effectiveness is more stable after 100 hours of exposure in electromagnetic radiation. On the other hand, when madder dyed silks were treated with this inhibitor, their light fastness was increased impressively at the first 200 hours; after that, the inhibitor treatment causes more severe deterioration to the dyed sample.

Inhibitor E provided protection in almost all dyed samples except the one dyed with safflower. It can be noticed that its effectiveness increases with the passing of the time, as in most of the cases the colour changes of the treated and non treated samples are the same at the first 100 hours and the resistance to light deterioration of the treated sample is observed later on.

Special attention is given to inhibitor F which is a combination of a UV absorber and an antioxidant, and generally shows good performance on most of the samples, except safflower dyed silk again. The ones dyed with madder and brazilwood showed no special improvement but at least their light fastness it not negatively affected. The cochineal dyed samples and the ones with dye combinations have shown an interesting improvement of their light fastness, not at the first period of exposure but at more extended time periods (200-400h).

Inhibitor G, also an inhibitor combination, had no good results in any of the samples. On the contrary, it seems that it increased the colour differences after exposure of all the samples.

Inhibitor H increased the light fastness of samples dyed with single dyestuffs, except safflower. The fading rates of madder, brazilwood and cochineal have improved significantly after treatment with this inhibitor combination and exposure to light, and especially when the time of exposure increases. With dye combinations the situation is more complex, as the fading rates show no stability during exposure.

Finally, inhibitor I which is also a combination of an absorber and an antioxidant showed an increase in lightfastness on madder, cochineal and combination 2 dyed samples but its performance is restricted to the first hours of exposure ;later on it fails to keep the good result. Its performance is considered poor on brazilwood, safflower and combination 1 dyed silks; the combination 1 samples show a negative effect after treatment with this inhibitor.

10.3.c Assessment of light fastness according to test No3 (50°C)

In this test the samples were exposed to intense light under higher temperature conditions, at 50°C. Each cycle of the experiment lasted for 250h and 400h and the exposed and non-exposed side of each sample was measured with a Minolta CR-221 chromameter with light source C, a 3mm diameter measuring area, and a 45° illumination angle. The meter was calibrated before each measuring session using a standard white plate. Colourimetric measurements and calculation of the colour differences between the exposed and non-exposed areas of the samples lead to the formation of the charts given in detail in *Appendix C, section C.4 and C.5.* The charts give the average colour difference that occurred after exposure of the samples in the two selected time periods. The results are summarised in Table 31.

Table 31. Colour change averages after 250 and 400 hours at 50ºC

		Exposure for 250 hours					Exposure for 400hours				
Treated samples		Av. ΔL*	Av. Δa*	Av. Δb*	Av. ΔE	St. Dev of ΔE	Av. ΔL*	Av. Δa*	Av. Δb*	Av.ΔE	St. Dev. of ΔE
Madder	blank	-0,67	10,92	-1,05	*11*	0,87	-1,56	11,21	-0,89	*11,55*	1,18
	A	1,03	-0,03	0,24	*1,95*	1,46	2,17	-0,49	0,53	*2,44*	1,74
	B	-0,53	0,55	0,80	*2,74*	1,46	1,65	-1,46	0,36	*2,58*	1,67
	C	0,07	0,39	1,52	*1,71*	0,61	0,90	0,067	1,71	*2,22*	0,24
	D	-0,43	-0,29	-1,01	*1,75*	0,49	0,96	-1,20	-1,02	*2,05*	1,62
	E	-0,16	0,12	0,14	*1,95*	0,70	0,48	-0,06	-0,12	*1,13*	1,02
	F	-0,26	0,47	0,18	*1,13*	0,59	-0,20	0,46	0,11	*0,84*	0,41
	G	-1,14	1,23	2,34	*2,98*	0,58	0,17	0,86	1,59	*2,16*	0,50
	H	0,22	-0,45	0,05	*0,85*	0,26	0,84	-0,37	0,31	*1,15*	0,30
	I	0,29	0,29	-0,16	*2,02*	1,05	0,68	-0,04	-0,99	*2,52*	0,29
Brazilwood	blank	-0,45	-0,84	0,67	*1,41*	0,24	-0,23	-0,55	0,84	*1,13*	0,20
	A	-1,64	-1,01	-0,39	*3,06*	3,09	-1,23	0,18	1,19	*2,47*	0,85
	B	-0,77	-0,85	0,70	*1,37*	0,38	0,61	-0,91	0,56	*1,90*	0,99
	C	-2,43	3,49	4,92	*6,52*	0,49	-1,64	4,33	5,39	*7,13*	0,33
	D	-0,11	-1,35	0,16	*1,42*	0,04	1,06	-0,34	0,31	*1,41*	0,27
	E	-0,38	-1,62	0,02	*1,80*	0,90	0,05	-1,56	-0,23	*1,69*	0,79
	F	-0,42	-0,82	0,78	*1,30*	0,25	0,13	-0,09	1,06	*1,14*	0,15
	G	-0,27	-1,12	0,58	*1,46*	0,18	0,61	-0,02	1,02	*1,22*	0,10
	H	-0,67	-2,38	-0,96	*2,66*	0,87	0,52	-1,76	-0,83	*2,02*	0,65
	I	-0,99	0,76	3,09	*3,41*	0,44	-0,81	1,27	3,34	*3,68*	0,33
Safflower	blank	-0,02	-1,33	-0,19	*1,40*	0,58	0,16	-1,96	0,47	*2,03*	0,36
	A	0,67	-3,11	-2,46	*4,08*	0,86	1,54	-4,54	-1,18	*4,97*	1,07
	B	-1,01	-0,53	-1,35	*1,93*	0,49	0,58	-2,29	0,35	*2,47*	1,15
	C	0,64	-2,05	-0,53	*2,35*	0,93	1,40	-2,95	-0,26	*3,35*	1,43
	D	0,02	-1,26	-0,59	*1,82*	0,58	0,44	-1,85	1,01	*2,30*	0,85
	E	0,77	-2,01	-0,27	*2,21*	0,45	0,70	-2,07	1,18	*2,61*	0,69
	F	-0,19	-1,47	-0,80	*1,89*	0,62	-1,83	-1,51	0,21	*3,48*	1,25
	G	0,08	-2,48	-0,86	*2,64*	0,38	0,69	-2,88	-0,13	*3,23*	1,97
	H	-0,18	-1,42	0,49	*1,72*	0,56	0,11	-1,63	1,76	*2,42*	0,25
	I	0,49	-2,29	-1,95	*3,14*	0,73	0,91	-2,72	-1,44	*3,32*	1,12
Cochineal	blank	0,05	-0,92	-0,85	*1,31*	0,50	0,41	-0,86	0,05	*1,09*	0,55
	A	0,85	1,86	0,30	*2,07*	0,62	1,47	1,84	1,15	*2,69*	0,85
	B	-1,08	-2,32	-0,21	*2,69*	1,02	0,34	-1,59	0,22	*1,70*	0,63
	C	-0,97	0,44	0,83	*1,49*	0,79	-0,42	1,33	1,84	*2,40*	0,62
	D	1,03	-0,26	-0,78	*1,33*	0,83	1,76	0,30	-0,25	*2,17*	0,27
	E	-0,47	0,01	0,04	*1,35*	0,90	0,42	0,67	0,50	*1,52*	0,40
	F	-0,40	-0,52	-0,30	*1,01*	0,49	0,78	0,88	0,49	*1,39*	0,52
	G	0,98	1,08	0,03	*1,49*	0,09	1,12	0,96	1,02	*1,95*	0,28
	H	-0,46	-0,33	-0,78	*1,11*	0,11	-0,16	0,32	0,21	*1,00*	0,57
	I	-1,30	0,56	1,40	*2,34*	1,52	-0,45	0,49	1,75	*2,03*	0,89
Combination1	blank	-0,32	0,42	0,33	*0,76*	0,32	-0,48	-0,01	-0,13	*0,98*	0,34
	A	1,43	-0,39	0,12	*1,51*	0,29	0,11	-0,51	-0,17	*2,06*	0,73
	B	-1,81	2,16	1,76	*3,36*	0,66	0,16	0,02	0,49	*0,92*	0,27
	C	-0,22	-0,34	0,59	*1,48*	0,22	-0,20	0,55	0,45	*1,57*	0,85
	D	-0,29	-0,30	-0,37	*0,79*	0,38	0,04	0,66	-0,22	*0,99*	0,42
	E	0,29	-0,14	-0,02	*1,02*	0,45	0,99	-0,54	0,1	*1,25*	1,18
	F	0,06	3,77	0,70	*4,32*	3,10	0,41	-0,38	-0,13	*0,90*	0,41
	G	-0,90	-0,41	-0,68	*1,30*	0,69	-0,45	-0,07	-0,35	*1,02*	0,41
	H	0,13	-0,78	-1,20	*1,75*	1,19	-0,03	0,35	0,135	*1,58*	1,03

Combination2	I	-0,83	0,36	0,02	*2,18*	0,66	-0,11	-0,67	0,46	*1,62*	1,15
	blank	-1,87	0,61	-0,51	*2,09*	0,91	-0,48	-0,01	-0,13	*0,98*	0,34
	A	1,17	-0,12	0,47	*1,63*	0,29	0,11	-0,51	-0,17	*2,06*	0,73
	B	-1,62	0,77	0,94	*2,20*	0,79	0,16	0,02	0,49	*0,92*	0,27
	C	-0,49	-6,37	0,20	*6,40*	0,58	-0,20	0,55	0,45	*1,57*	0,85
	D	-0,74	0,04	-1,12	*1,48*	0,26	0,04	0,66	-0,22	*0,99*	0,42
	E	0,02	0,17	0,18	*2,19*	1,47	0,99	-0,54	0,1	*1,25*	1,18
	F	-0,17	-0,25	-0,73	*0,97*	0,38	0,41	-0,38	-0,13	*0,90*	0,41
	G	-0,65	0,77	-0,27	*1,15*	0,37	-0,45	-0,07	-0,35	*1,02*	0,41
	H	-0,55	0,31	-0,48	*3,01*	1,89	-0,03	0,35	0,135	*1,58*	1,03
	I	-0,78	0,86	0,58	*2,02*	1,95	-0,11	-0,67	0,46	*1,62*	1,15
Combination3	**blank**	-0,68	-1,86	-1,29	*2,43*	0,15	-0,22	-1,40	0,16	*1,54*	0,26
	A	0,56	0,83	-1,71	*2,46*	1,51	1,40	1,35	-0,62	*2,21*	0,45
	B	-1,020	-1,693	0,057	*2,01*	0,55	0,12	-0,78	0,72	*1,43*	0,65
	C	-1,87	0,18	-0,05	*2,41*	1,27	-0,94	0,64	0,65	*1,54*	0,85
	D	-0,06	-1,99	-1,84	*2,77*	0,25	0,16	-1,57	-0,38	*1,68*	0,59
	E	-0,84	-1,11	-1,12	*2,35*	0,20	0,17	-0,72	-0,04	*0,77*	0,35
	F	-1,24	-0,30	-0,38	*1,53*	0,75	-1,16	0,11	0,64	*1,49*	0,44
	G	0,09	-1,03	-1,47	*1,86*	0,53	0,68	-0,35	-0,22	*1,14*	0,37
	H	-0,55	-1,42	-0,71	*2,28*	0,49	-0,18	-0,65	0,16	*1,33*	0,67
	I	-0,59	-0,49	-1,39	*2,33*	0,63	-0,08	-0,58	0,76	*2,75*	2,00

What was generally observed was that the samples faded less at 50°C than at room temperature, as used in the two previous light fastness tests. This may be attributed to the lower levels of humidity in the oven chamber due to the rise of temperature. Also as the whole experiment was restricted in the closed chamber, the levels of oxygen may also have diminished a little. As explained before, environmental humidity is a fundamental factor affecting the light fastness of several natural dyes and it has been shown before that fading is accelerated on silk when humidity is raised. Also anoxic or low oxygen environments are providing less oxygen to photochemical reactions and therefore the photo-oxidation step is retarded. On the other hand, textiles are hygroscopic materials and higher humidity is more important than in other materials in order to maintain their mechanical properties. As this was considered an important observation and it was essential to base the above-mentioned hypothesis on relevant test results, a fourth light fastness test was necessary and performed as explained above.

When treated with photodegradation inhibitors, the silk samples showed in some cases very promising results as it seems that they work much better at higher temperature and low humidity levels. Madder dyed silk proved again to have the better light stability when treated with

the selected additives although, as the time of exposure is increased, some of the inhibitors start to lose their effectiveness. However, it was noticed that additive G did not show such good results at the first hours of exposure, where later (400h) it increased the light fastness of silk where the others were starting to fail. Using the *t*-test, the protection provided by inhibitor G is statistically significant with t=12,7 and p=0,0002 at 5% significance level. Additive F showed a stable performance during all exposure times and this too is statistically significant with t=14,9 and p=0,0001 at 5% level.

Samples dyed with brazilwood and treated with the several inhibitors have given no good results. Although the non treated sample performs much better than it did at room temperature, when treated with the additives its light sensitivity is increased. What was also noticed is that inhibitors that seem to work satisfactorily with this dyestuff at room temperature, such as the inhibitor combination H, are now failing to protect the textile from fading and over and above are causing more fading. In the case of inhibitor H, these results are statistically significant at both times of exposure (250h and 400h), with t=-239 and p=0,075 and t=-2,25 and p=0,087 respectively, at 5% level of significance. An example is given in *Figure 45*, where the chart shows the magnitude of the colour difference, in the form of vertical columns, of the treated samples at room temperature and at 50°C when exposed for 400h.

Silk samples dyed with safflower have shown before very low light fastness and none of the inhibitors has succeeded to increase it. With the rise of temperature the non treated sample proved to resist more the light induced colour changes. One needs to notice that at room temperature, for 400h of exposure the non treated sample showed ΔE of 33.11 units, where at the same exposure time (400h) at 50°C the colour difference of the non treated sample was ΔE 2.019 units. The application of inhibitors in this case too does not show any important improvement. Inhibitor H appears to provide a slight increase of light fastness on safflower dyed samples and this was not happening at room temperatures. This suggests that this inhibitor combination is presenting a synergistic effect in these environmental conditions. However,

Student's *t*-test for these results shows that they are not statistically significant with t=-0,685 and p=0,53 at 5% significance level.

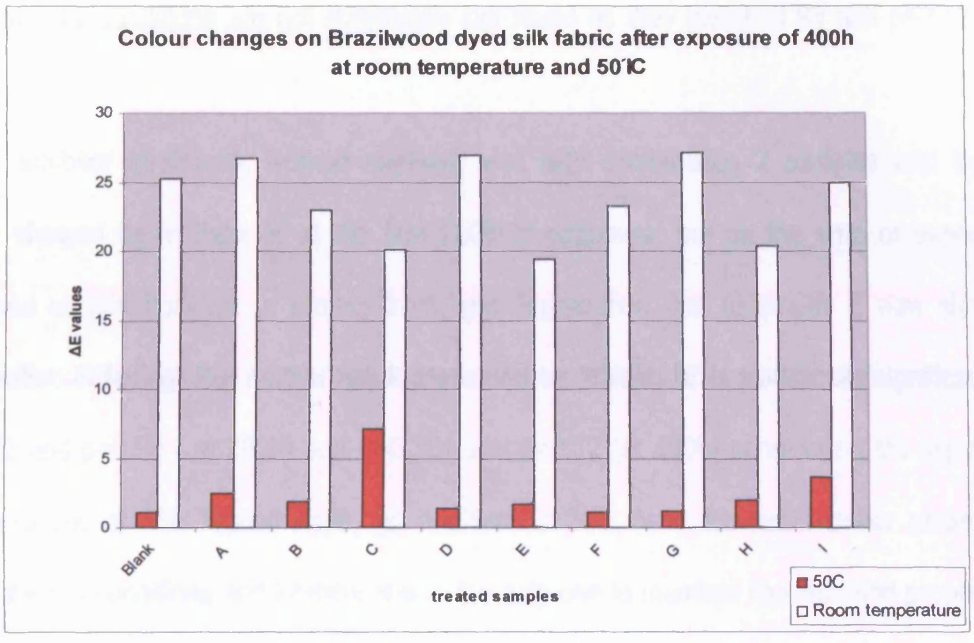


Figure 45. The colour difference of brazilwood samples when exposed for 400h at room temperature and 50°C

With cochineal dyed silk, inhibitors E, F and H appear to give good results providing photo-protection of the samples to a considerable degree, but inhibitors A, B and I accelerate fading. Here also, inhibitor F shows good performance at 50°C but it did not have the same ability when evaluated at room temperature. However, the positive results presented by inhibitors E, F and H are not statistically significant, with t=-1,07 and p=0,34 (inhibitor E), t=-0,681 and p=0,53 (inhibitor F) and t=0,196 and p=0,85 (inhibitor H) at 5% level. Similarly, the negative results presented by inhibitor A, B and I are not statistically significant with t=-2,74 and p=0,052 (inhibitor A), t=-1,26 and p=0,28 (inhibitor B) and t=-1,56 and p=0,19 (inhibitor I) at 5% level of significance.

Samples dyed with combination 1 in general show an improved light fastness with inhibitors D, E and G but the change is not so impressive. Inhibitor D appears to work better under these environmental conditions than at room temperature but the improvement is not statistically significant, with t=-0,817 and p=0,94 at 5% level of significance. Inhibitor A, B and F accelerate fading on these samples. It has to be mentioned that inhibitor F performed better at

room temperature. This gives an antithesis of what was observed before with this inhibitor (F) when used on cochineal dyed samples. However, the results presented by inhibitor F under these environmental conditions are not statistically significant as they give t=-1.98 and p=0,12 at 5% level.

Inhibitor treatments worked relatively well with combination 2 samples with the best results showed by inhibitor E at the first 250h of exposure, but as the time of exposure is increased all inhibitors fail to protect from light degradation and especially E now shows an acceleration in fading. But neither result presented by inhibitor E is statistically significant, with t=-0,972 and p=0,93 (at 250h) and t=-0,381 and p=0,72 (at 400h) considering the significance level was set at 5%. Nonetheless, all additives in this case too work better under these environmental conditions and inhibitor H was the only one to maintain its stabilizing properties as the time passes. An example is given in *Figure 46*, where the colour difference is presented after exposure for 250h at room temperature and at 50°C.

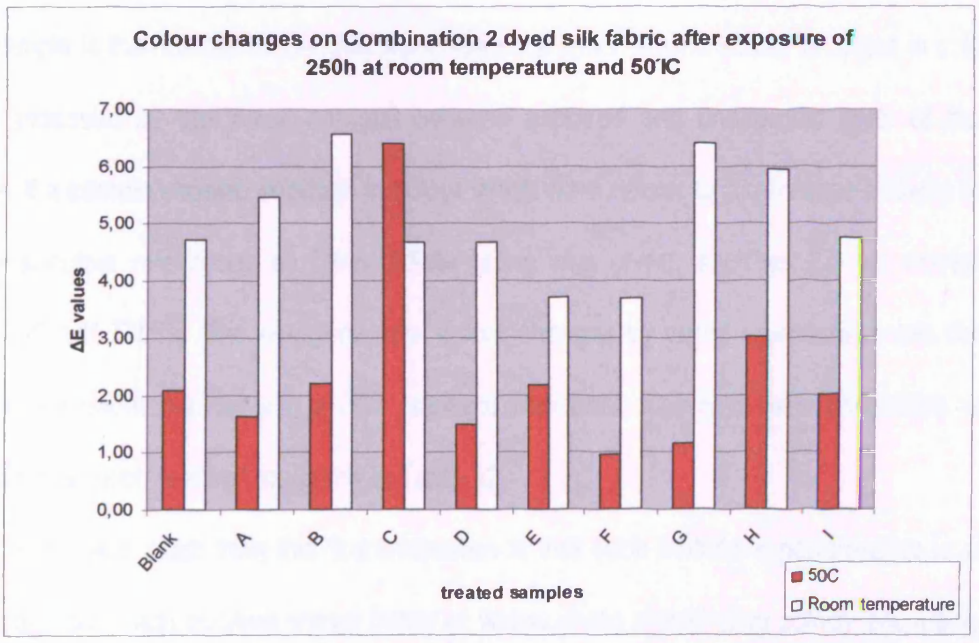


Figure 46. The colour difference of combination 2 samples when exposed for 250h at room temperature and at 50°C

Combination 3 dyed samples showed the best light stability of all dye combinations and when treated with inhibitors their light fastness in general is improved. The best results were

identified in samples treated with inhibitors E and H but it has to be mentioned that as the time of exposure increases the protection from light degradation provided by the additives is reduced. However, in both these cases, the differences are not statistically significant, with t=0,504 and p=0,64 for inhibitor E and t=0,496 and p=0,65 for inhibitor H at 5% significance level.

10.3.d Assessment of light fastness according to test No4 (changing humidity levels)

In this test as already described all parameters were kept stable and only one was changed through three experimental cycles. This parameter was humidity, which was set at three different levels, low (30±2%RH), medium (50±2%, representing the controlled environment of a museum) and high (80±2%). Temperature was kept stable at 35°C, and all samples were exposed for 100hours.

The evaluation of the test results was firstly done using the blue wool standards exposed together with the samples and a grey scale as was done in test No1. The light fastness grade for each sample is the number of the blue wool reference which shows similar changes in colour and this is assessed by the visual contrast between exposed and unexposed parts of the same sample. If a sample showed changes in colour which were nearer to a reference midway between two consecutive references an intermediate rating was given, such as 2-3 for example (BS 1006:1990, UK-TN/5). The assessment of colour changes by visual examination was done in a colour assessment cabinet with a D65 standard illuminant. The light fastness grades resulting from this evaluation method are given in Table 32.

What was clear from this first evaluation is that each inhibitor's performance is affected by humidity and each additive shows better or worse photo-stabilization activity according to the humidity level adopted in each cycle.

Table 32. Light fastness grades after exposure at three different humidity levels.

	Light fastness grades					
Inhibitor treated	***Brazilwood***			***Cochineal***		
samples	30%RH	50%RH	80%RH	30%RH	50%RH	80%RH
Blank	1-2	1-2	2	4	3	3
A	2	1-2	1-2	4	3-4	2-3
B	2	1-2	2	4	3-4	3
C	1-2	1-2	2	4	3-4	3
D	1-2	2	1-2	5	3-4	2-3
E	2	1-2	2	5	3-4	2-3
F	2	1-2	2	4-5	3-4	2-3
G	1-2	1-2	1-2	4	3-4	2-3
H	2-3	2	2	5	3-4	3
I	2-3	2	1-2	4-5	3-4	2-3

The blank sample, as expected, shows better colour fastness when humidity is kept at lower levels while fading is accelerated in high humidity.

In general treatments with some inhibitors seems to increase the light fastness mostly when humidity is low (30%RH) and in some cases this improvement is also noticed in higher humidity levels. In order to have a more quantitative evaluation, colourimetry was also used with the use of a *Spectro-color* colourimeter with light source D65, a 3mm diameter measuring area, and a 10° illumination angle. The meter was calibrated before each measuring session using standard white and black plates. For these measurements the CIE L*a*b* system was used.

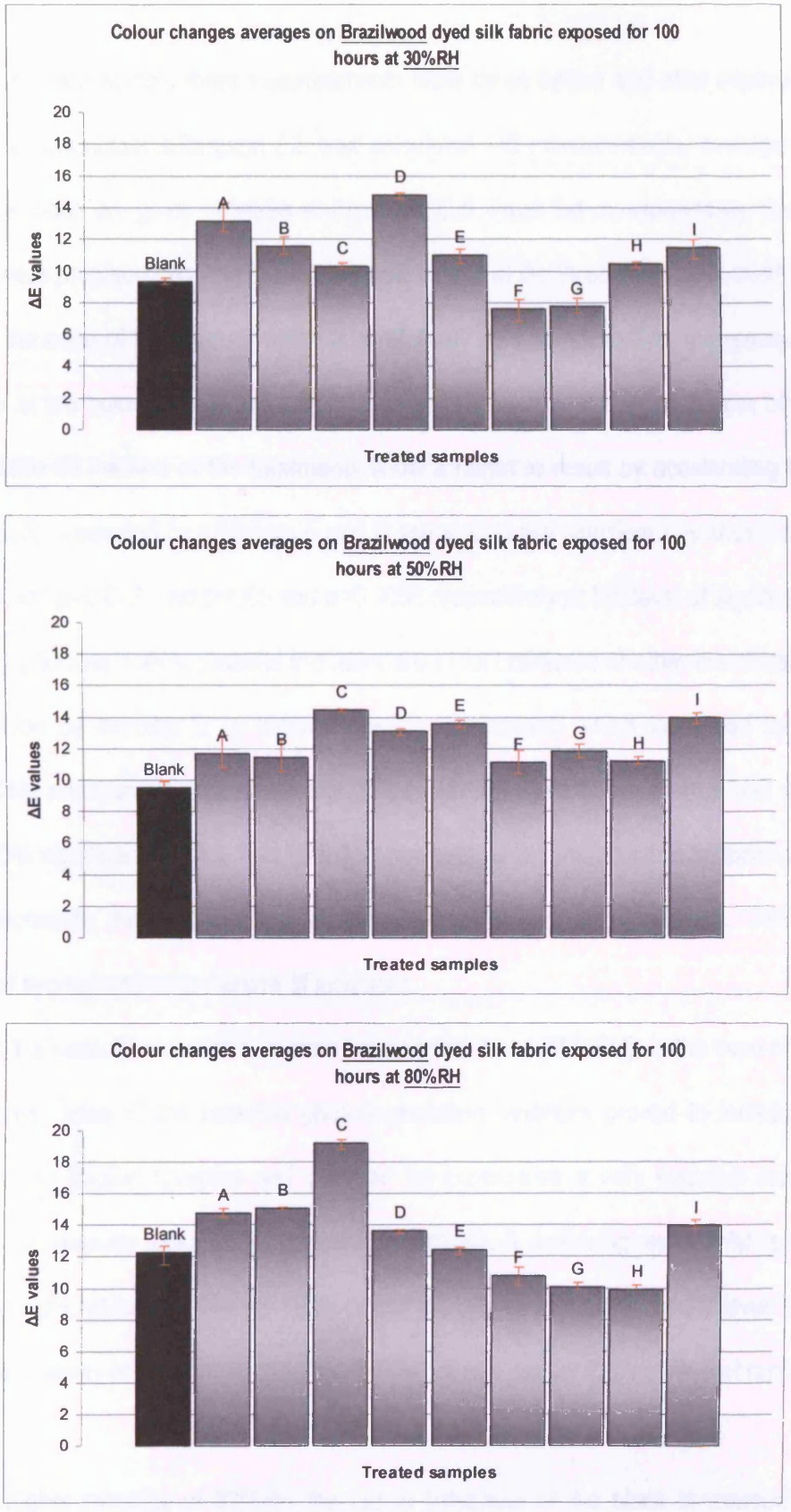


Figure 47. Colour changes averages on brazilwood dyed silk fabric exposed for 100hours at three humidity levels

From each sample three measurements were taken before and after exposure and the magnitude of the colour difference ΔE was calculated. All measurements, averages and their standard deviation are given in tables in *Appendix C.6*. From the measurements, the graphs of *Figure 47* were prepared showing the average ΔE values at the three different humidity levels.

In the case of brazilwood, which is a relatively light sensitive dye, the results are rather puzzling as at low humidity only two inhibitors (F and G) improve the light fastness of the treated samples, while all the rest of the treatments show a negative result by accelerating fading. The positive results presented by inhibitors F and G are statistically significant as shown by the *t*-test with t=4,25 and p=0,013, and t=4,65 and p=0,0096 respectively at 5% level of significance. It has to be mentioned that both successful inhibitors are in fact mixtures of other inhibitors. The worst result is given by inhibitor D (a hindered amine antioxidant) which increased fading at low humidity. This result too is statistically significant with the *t*-test giving t=-16,9 and p= less that 0,0001 at 5% significance level. This inhibitor, however, is a component of inhibitor combination G which increases the light fastness at the same environmental conditions. This is a clear indication of synergism in this mixture of inhibitors.

As the humidity is raised to a more intermediate level (50%RH), in the case of brasilwood dyed samples, none of the selected photodegradation inhibitors proved to increase the light fastness of the treated samples and this can be considered a very negative result, as this humidity level is usually indicated for museum collections. A surprising result is that presented by the blank sample, which showed the same colour change as in lower humidity level. This means that the light stability of the brasilwood dyed silk is not affected by the increase of humidity at this level.

At higher humidity of 80%RH the fading behaviour of the blank brasilwood sample is clearly affected and the colour change is increased. In this case three inhibitors seem to protect silk from fading, and these are inhibitor combinations F, G and H. The best results are given by

inhibitor H, a combination of a benzotriazole absorber and a polymeric hindered amine antioxidant, while the worse results, expressed by the acceleration of fading, is given by inhibitor C, which is nonetheless a component of the successful combination H. This observation reinforces for one more time the synergism discussed before. The positive result presented by inhibitor H at this humidity level is statistically significant as the *t*-test gives t=5,72 and p=0,0046 at 5% α-level. Moreover the negative effect observed by inhibitor C is also statistically significant with t=-15,8 and p=less than 0,0001 in the *t*-test at 5% level of significance.

The most important observation in all three cycles of this test on brasilwood samples, is that inhibitor combination H is the only one showing stable results in every humidity level tested. In all three cases, the samples treated with inhibitor H show the same colour difference after exposure for 100hours at 35ºC temperature. This can be shown in the graph of *Figure 48* and gives an advantage to this additive in comparison to the others, although at 50%RH it is not seen to be as successful, as the blank sample shows less colour change. Relevant graphs for all selected inhibitor treatments in comparison to the blank samples in all three cycles are presented in *Appendix C.7.*

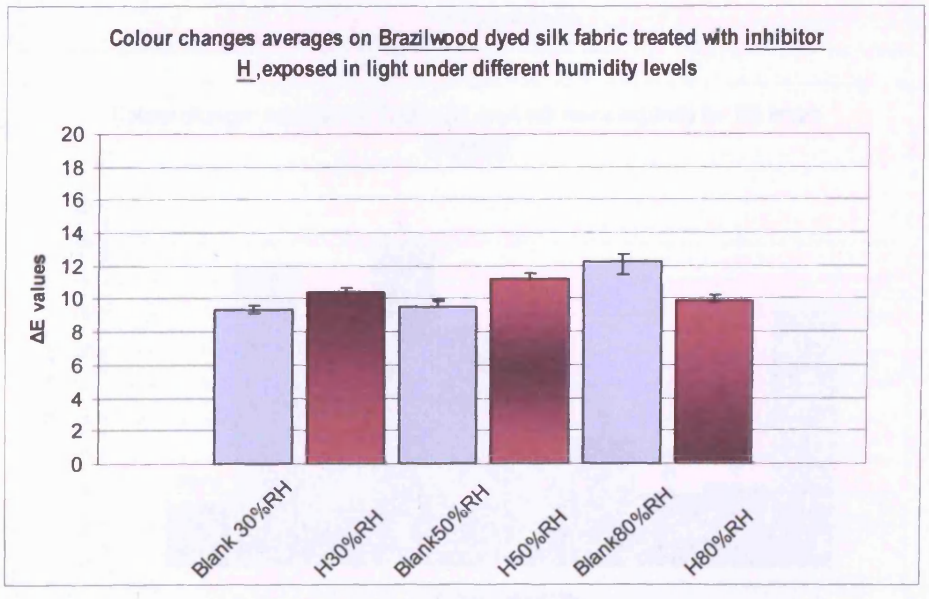


Figure 48. colour changes averages on brasilwood dyed silk fabric treated with inhibitor H, exposed in three different humidity levels in comparison to the non treated sample at the same environmental conditions.

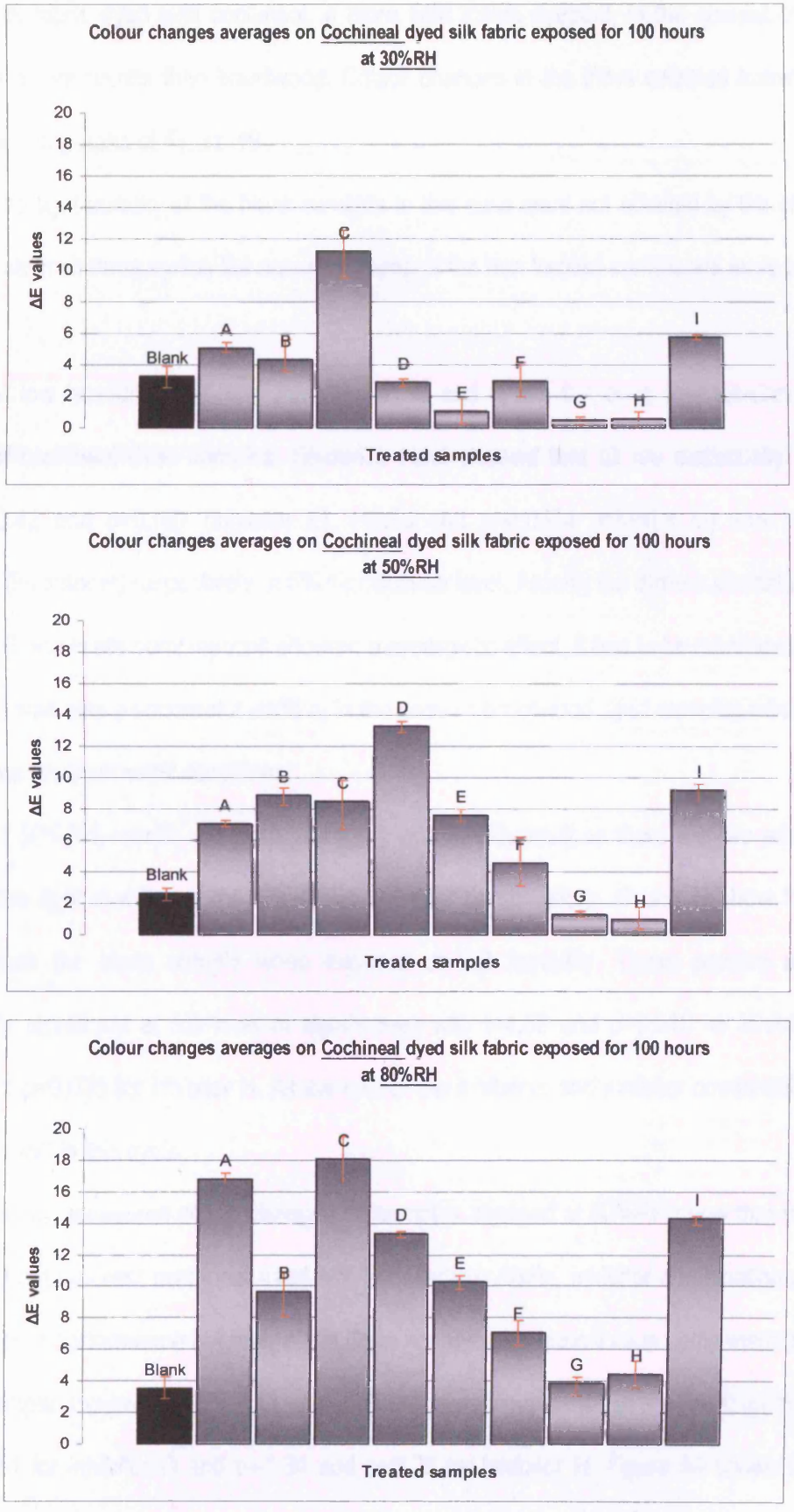


Figure 49. Colour changes averages on Cochineal dyed silk fabric exposed for 100hours at three humidity levels

Silk fabric dyed with cochineal, a more light stable dyestuff, in the context of this test showed different results than brasilwood. Colour changes in the three selected humidity levels can be seen in graphs of *Figure 49.*.

The light stability of the blank samples in this case were not affected by the changes of humidity, as in all three cycles the colour changes of the non treated sample are more or less the same.

At low humidity (30%RH), inhibitors E, G and H are the ones that increase the light stability of cochineal dyed samples. Student's *t*-test showed that all are statistically significant giving t=3,42 and p=0,027 (inhibitor E), t=6,83 and p=0,0024 (inhibitor G) and t=5,85 and p=0,0043 (inhibitor H) respectively at 5% significance level. Among the three successful additives inhibitors G and H are combinations showing a synergistic effect. It has to be mentioned here that inhibitor G was also a successful additive in the case of brasilwood dyed samples when exposed at the same environmental conditions.

At 50%RH, results are more promising with this dyestuff as there are two additives that improve the light stability of the silk fabric. Inhibitor combinations G and H show less colour change than the blank sample when exposed at this humidity. These positive results are statistically significant at 5% level of significance with t=4,56 and p=0,010 for inhibitor G and t=3,44 and p=0,026 for inhibitor H. All the rest of the inhibitors and inhibitor combinations give a negative result in this cycle.

Finally, measured colour changes on samples exposed at 80%RH show that most of the inhibitors fail to protect cochineal dyed silk from fading. Again, inhibitor combinations G and H show the best performance but their effect does not seem so beneficial in comparison to the non treated sample. However, the results are not statistically significance at 5% level, giving t=-0,545 and p=0,61 for inhibitor G and t=-1,34 and p=0,25 for inhibitor H. *Figure 50* shows the colour changes of the samples treated with inhibitors G and H in comparison to the non treated sample.

Relevant graphs showing the performance of each inhibitor against the blank sample in the same environmental conditions are given in *Appendix C.7.*

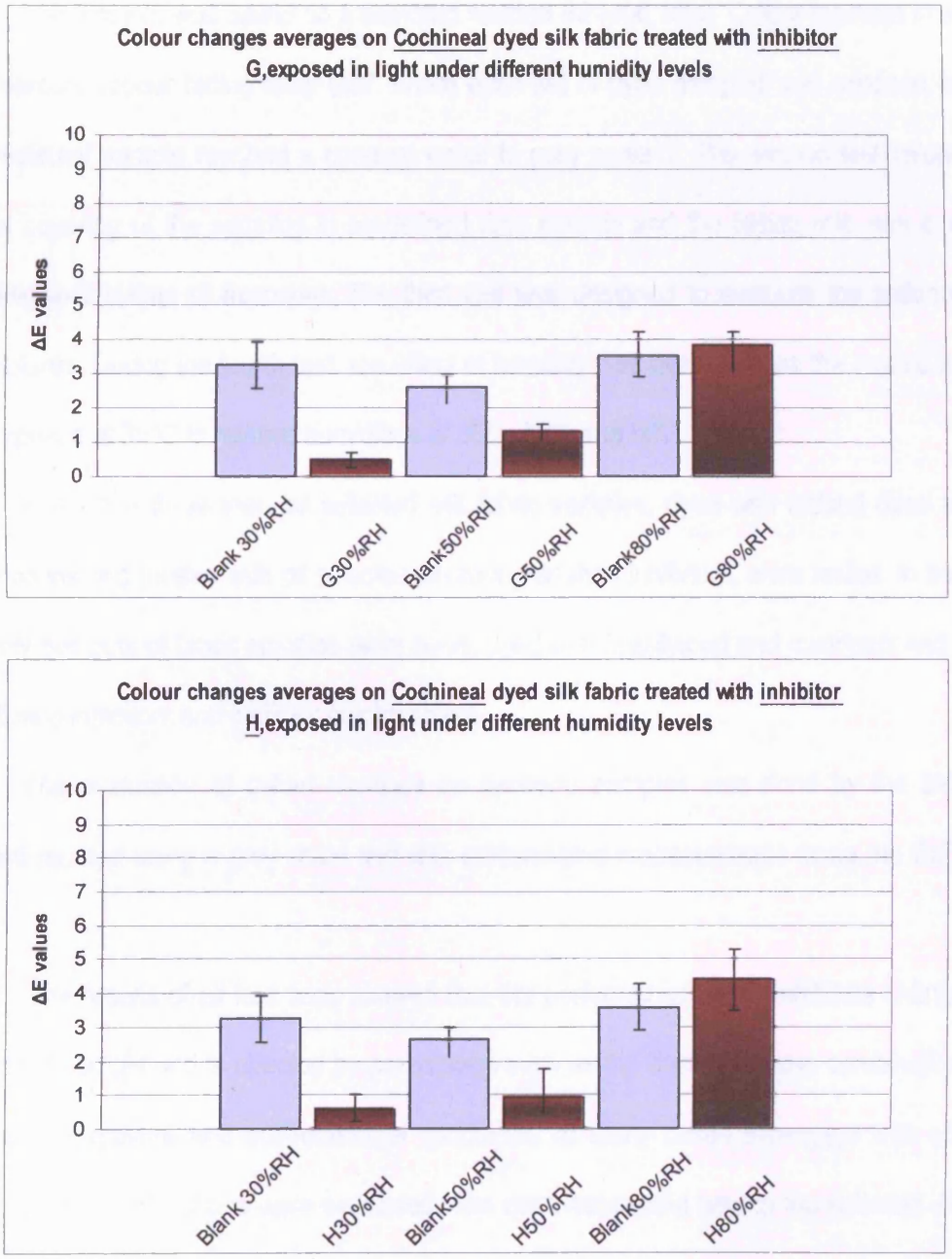


Figure 50. Colour changes averages on cochineal dyed silk fabric treated with inhibitor combinations G and H, exposed to light under the three selected humidity levels in comparison to the non treated samples at the same environmental conditions.

Section summary

Four light fastness tests were performed. Each test was designed according to the preliminary results given by its preceding test.

The first test was based on a standard method BS1006:1990 "Colour fastness to artificial light: mercury vapour fading lamp test" where each set of dyed samples was exposed until the most resistant sample reached a contrast equal to grey scale 3. The second test involved the gradual covering of the samples in predefined time periods and the fading rate was evaluated according to the time of exposure. The third test was designed to evaluate the action of high temperatures. During the fourth test, the effect of humidity was evaluated, as the treated samples were exposed at 35ºC to relative humidities of 30%, 50% and 80%.

In the first three tests all selected silk fabric samples, dyed with natural dyes and dye combinations and treated with all selected photodegradation inhibitors, were tested. In the fourth test, only two sets of fabric samples were used, dyed with brasilwood and cochineal and treated with all nine inhibitors and inhibitor combinations.

The evaluation of colour changes on exposed samples was done by the blue wool standard method using a grey scale and with colourimetric measurements using the CIE L*a*b* system.

The results of all four tests showed that the performance of the inhibitors changes with every dyed sample and is affected by parameters such as the dyestuff or dye combination used, the time of exposure and environmental conditions. In many cases synergism was observed when inhibitor combinations were evaluated. The most successful among the selected inhibitors can be considered inhibitor combination H, the mixture of a benzotriazole absorber and a hindered amine antioxidant, not only because it increased the light fastness of most of the dyed samples, but mostly for the consistency of the results in all four tests.

11. Discussion

The primary objective of this research was to evaluate not only the ability of the selected inhibitors to increase the light fastness of particularly dyed silks, but also the possibility of their being used as conservation treatments for historic textiles.

As a conservator myself, I sense that for the introduction of any new material into the conservation field, one has to think a lot about the requirements, the expectations and the hesitation from the conservation point of view. In other words, research planned to lead to the design of a new conservation treatment has to consider the conservator and conservation ethics. Until now not much consideration has been given to this matter and there is still some conflict between conservators and conservation scientists that in the development of new treatment methods for conservation, the combination of scientific theory and practical technique is rarely considered (Tennent 1992, Ward 1986). Apart from the literature review on this matter and personal experience, the opinion of other conservators working on textile conservation and facing photodegradation problems was also considered *(see chapter 6 and section 11.4)*.

The results from the accelerated aging tests are sometimes promising but most of the times are puzzling and undoubtedly open a new field of research, but how much of this can be considered in conservation? Having in mind the above and with the acceptance that new treatments should always be evaluated in the context of the interminable battle of the conservator with time, the following discussion concerns both the performance of photodegradation inhibitors and questions of conservation ethics. The presentation and the evaluation of the experimental results as presented in *Chapter 10* , more or less follow the standards set by industrial testing and

applications, but the whole methodology of this research as presented in *Chapters 7 to 10* shows a different approach on the subject, from a conservation point of view and the discussion of these results is proportionate. The following discussion includes many contradictory parameters which are given separately in order to understand the complexity of the situation when all these variables will be put together.

11.1 Discussion on applicability of selected photodegradation inhibitors

An important concern during this study was the application effects of the selected inhibitors on the textile's overall properties, if they are designated for conservation purposes on historic valuable objects.

The first concern that arises is the selection of solvent. All selected inhibitors in this research were non water soluble. On the other hand in modern polymer industry, it seems that the water soluble inhibitors are preferred as they can be combined to the dying procedures of the new lightfast fabrics used for outdoors furniture, automobile upholstery and UV protecting clothing (Krichevsky *et al* 1990, Waters *et al* 1980, Carr *et al* 1985, Cegarra *et al* 1972). The exclusion of water soluble inhibitors in this research, from the preliminary testing, was a conscious choice which was also combined with other prohibitive characteristics of the excluded additives (colour, toxicity, availability). The use of water is very often restricted in textile conservation due to its uncontrollable effects to fibres, dyes and other construction materials.

Several different organic solvents were tested in the context of this study and the additives were selectively dissolved in them. The choice of these solvents was based on their use in textile conservation for several purposes, taking into consideration their limitations, disadvantages or failures. It seems that other researchers experimenting with photo-inhibitors do not give special attention to the properties of the solvent used, as they are dealing with new fabrics. The preliminary testing in this research suggested that the use of alternative solvents or

solvent mixtures may deliver valuable solutions concerning ease of application in the laboratory, safer working environment, better absorption of the additives by the fibres or lower cost. For example, treatment with photodegradation inhibitors dissolved in acetone would be quicker, because of the volatility of the solvent and the additive would be better absorbed by the fibres. Ethanol, on the other hand, provides clear solutions and less colour change to the treated textile.

The selection of tetrachloroethylene for further testing was made under conservation restrictions but still its use is questionable due to its toxicity and high cost. On the other hand, all the selected additives dissolved readily in this solvent without any noticeable side effects such as dye bleeding or fibre disfiguration. It has to be mentioned that the most successful inhibitor combination, inhibitor H, having the best performance in light stabilization of the dyed silks tested in this research, was soluble only in this solvent. Then again as tetrachloroethylene does not swell natural fibres it does not provide adequate introduction of the inhibitors into the fibres , as water may do, and this may have effected their performance. That is why Becker *et al* (1987) used N,N-dimethyl formamide (DMF) as solvent in their experiments on silk fabrics as this solvent has very good fibre swelling characteristics. In that case they needed to add chloroform or xylene to the DMF in order to dissolve some of the additives, as not all of them were easily dissolved. All the aforementioned solvents are avoided in textile conservation due to their toxicity and damaging effects to fibres. Many fragile textile objects and applied decorations would be dissolved and destroyed with the use of these solvents. On the other hand, it was observed under the microscope that inhibitors were not readily absorbed by the fibres, as their particles were visible on the outer surface of the fibres after application, and this may be due to the selection of an organic solvent instead of water.

The concentration of the inhibitor when introduced into the fibres was another factor of interest and after absorption measurements it was noticed that some inhibitors had been absorbed and retained in the fibre structure more than others. In fact the hindered amine

Chimassorb 944 and the two inhibitor combinations (F and H) that include this hindered amine, showed the higher absorption levels on the silk fibres. From the inhibitors mentioned above, inhibitor combination H showed a general satisfactory behaviour throughout the light fastness tests and this may be accredited to the higher concentration of the inhibitor in the fibres. The amelioration of the light protection provided by inhibitors to fibres when the concentration of the additives is increased is also noticed by other researchers (Cegarra *et al* 1972, 296).

The application of the inhibitors by immersion is the general method used by researchers, and it seems likely that it provides uniform absorption by the fibres (Becker *et al* 1989, 99, Carr *et al* 1985, 51, Thorson 1989, 33). The samples after immersion are left flat to dry by evaporation as this is the practice taken during solvent cleaning in textile conservation. This may be the reason why the observed uptake was relatively high in comparison to other research. Becker *et al* (1987), for example, used a padder machine after immersion to remove excess solution from the fabric and their samples were placed on pin frames to dry. Carr *et al* (1985) and Waters *et al* (1980) used a dyeing machine to treat their samples at raised temperatures. These methods could not be used in this study as they would never be used in textile conservation.

Finally the effects on the colour of the fabric after treatment do not seem to be ideal as there is some colour change after application, especially on pale colours. This fact does not seem to trouble other researchers as they mention that the solutions of inhibitors are usually colourless or nearly colourless but there is no attention given to the treated samples before exposure to electromagnetic radiation. This is of course because they do not intend to use them in the conservation field where final appearance, after treatment, is extremely important and the conservator does not want to interfere with the originality of the object in any way. The only concern is focused by two researchers, de la Rie (1988) and Bourdeau (1988) when they were setting up their criteria for the selection of photodegradation inhibitors in acrylic surface coatings

and varnishes used in paintings. Just the same, the measured colour change on the treated samples in this study was not noticeable to the naked eye.

Changes in the mechanical properties of the treated textile is also of major concern. Some of the selected additives seem to causes changes in the breaking strength of the silk fibres either by increasing or reducing it, although these results are not statistically significant and therefore can be considered negligible. Elongation on the other hand is negatively affected in every case and a corresponding change in flexibility was also observed. Any substantial change of mechanical properties after treatment must be regarded with caution, but an increase in mechanical strength is most of the time welcomed. There are also many cases that additives are used in conservation exactly for this reason, such as consolidants. Photodegradation inhibitors that increase the breaking strength of silk fibres, such as inhibitor combination H, can thus be considered successful.

On the contrary, the induced changes in flexibility, as expressed by the reduction of elongation properties of the fibres after treatment, can be considered an important disadvantage. As far as silk fabrics are concerned, flexibility is one of their most important properties and very often affected by deterioration factors, such as photodegradation, and by several treatments such as finishes during production. In conservation, many if not all treatments including additives on silk fibres have proven to cause changes in elongation, such as the use of adhesives or consolidants.

Therefore the main points to be considered in relation to the induced changes of mechanical properties are how much change is observed, in which direction this change is focused (increasing or reducing strength) and how this change is evaluated in comparison to the benefits accomplished by the treatment in other sectors (photo-protection).

11.2 Discussion on performance of photodegradation inhibitors

The experimental results as presented in detail in *Chapter 10* showed primarily that every dyestuff had reacted differently to inhibitor treatments and this shows that the light fastness of the samples was affected by the dyestuff characteristics and not by the type of fibres, as in all cases the same cultivated silk fabric was used. What was observed in general is that the more light fast natural dyes such as madder and cochineal benefit from inhibitor treatment although some inhibitors fail to increase the light stability of even these samples. This observation is supported by the findings of Coleman and Peacock (1958) who reported that UV absorbers usually have better results on more light fast dyestuffs because low light fastness dyes are photodegraded by visible light too which is not absorbed by the inhibitors. The best results of all the dyed samples were shown by the ones dyed with madder. All selected inhibitors seem to provide protection to a certain extent to madder dyed silk.

On the other hand safflower dyed samples showed very intense fading under light exposure and none of the inhibitors increased their light fastness to any considerable degree. Safflower is one of the most light sensitive natural dyestuffs and it has the lowest lightfastness of all the dyes in this study. It has to be remembered though that safflower was the only dye applied without a mordant. The presence of mordants has been proved to have a positive effect both in light and wash fastness of textiles.

Samples dyed with dye combinations are far more complicated than the ones dyed with one dyestuff alone and the results of the inhibitor treated samples have no clear trend. Some inhibitors increase the light fastness and some not but their effectiveness is different to every dye combination. This confirms the primary hypothesis that dye combinations usually found on historic textiles need much more investigation and testing, as the problems arising are far more complicated than the theoretical approach of testing materials for modern purposes. As was pointed out by Moura *et al (*1996) in their review, dye mixtures generally have lower light fastness

than each of the dyes included in the mixture and this may be attributed to either excited state energy transfer form one dye to the other or creation of singlet oxygen by the dye components. It is observed though that the fading of one dyestuff is affected by the photochemical behaviour of the other dyestuffs present in the mixture.

From the three dye combinations selected, according to the dye identification results of the original historic samples, combination 1 and 3 have the highest light fastness and the best performance when treated with inhibitors. This may be due to their composition as combination 1 consists mainly of madder (97,5%) which proved to have the better performance when treated with inhibitors, of all other dyestuffs. Combination 3 also consists mostly of a relatively fast dye, cochineal (83%). Both dye combinations 1 and 3 include tannin in their synthesis. On the other hand, combination 2 also contains mainly madder (99%) but the inhibitors have no beneficial results and in some cases the fading is increased after treatment. This dye combination also includes lowson and maybe this is the ingredient that does not work well with the inhibitors. On the contrary, the blank sample dyed with combination 2 shows quite good light stability in comparison to the other non treated samples dyed with dye combinations, and this is maybe due to the high concentration of madder.

The effect of photodegradation inhibitors on the fading rates of the dyed samples was of importance in this study and that is why several exposure times were tried on the samples. What was generally observed was that some of the inhibitors like inhibitor E (the antioxidant Chimassorb 944) and F (a combination of an absorber and an antioxidant) showed little effectiveness in the first hours of exposure whereas they work better over longer exposure times. This can be compared to a previous observation form Carr *et al* (1985), that some promising combinations of absorbers and antioxidants when used on non dyed wool, initially showed a photo-bleaching which was then followed by yellowing of the wool fibres. This may lead us to the hypothesis that these two inhibitors are mainly working as antioxidants and they need more time

to function. In the case of inhibitor E (an antioxidant), UV light is not absorbed or screened by the additive and its function as photodegradation inhibitor starts when photo-oxidation is starting to occur. Although in inhibitor combination F a UV absorber is included, it does not work satisfactorily by absorbing electromagnetic radiation in the first stages of photodegradation and the mixture starts to work later.

Others on the contrary, like inhibitor B (a benzophenone absorber), inhibitor C (Tinuvin 327, a benzotriazole absorber) and inhibitor D (Tinuvin 770, a hindered amine antioxidant) show good performance in the first hours of exposure whereas later their fading rate either follows the fading rate of the non treated sample or accelerates fading. The same observation was made by Thorson (1990) when she tested photodegradation inhibitors on dyed wool fabric over several time periods. This may be due to the attenuation of the absorbing ability of the UV absorbers, or the degradation of the inhibitors which sometimes affects negatively the light fastness of the dyed silk. From the above mentioned inhibitors, Tinuvin 327 was also tested by Bourdeau (1988) in acrylic surface coatings and showed a good performance and long lived effectiveness. This leads us to the conclusion that the combination of the inhibitor and the substrate fibre and dyes used, is affecting its stability over aging.

Finally there are cases where during the first hours of exposure the treated samples show no improvement in their light stability, but as the exposure time increases the inhibitors start to perform better, and the light fastness of the samples increases significantly. This happened with inhibitors G, H and I which are all combinations of a UV absorber and an antioxidant. This may be attributed to the function of the absorber to primarily absorb UV radiation and then start to act as a quencher in accordance with the antioxidant.

The performance of the selected inhibitors is also affected by temperature. The temperature selected was 50°C, which is not an extreme level but an achievable temperature in non ventilated closed display cases in warmer countries in the summertime, especially when

direct sunlight is passing though a window glass. Also it was suggested by Becker *et al* (1989) in their study of inhibitors tested on silk fabric under light and heat experiments that inhibitors would perform better in more realistic conditions. These researchers tested the inhibitor treated silk at 150°C and found this temperature unrealistically high for evaluating the thermal stability of the selected additives (Backer *et al* 1989, 106).

What was generally observed was that the non treated samples dyed with natural red dyes and dye combinations showed a better resistance to light degradation under these conditions and this is maybe attributable to the lower levels of humidity achieved by the rise of temperature. The effect of humidity in the light fastness performance of fibres is of great attention when testing textiles for light fastness. As Allen (1994) noted, the absorbed moisture usually swells the polymer chains of hygroscopic natural fibres, and helps oxygen to disperse more easily though the medium. Also the sealed oven chamber may have restricted the supply of oxygen and this may have caused retardation of some oxidation reactions.

On the other hand it has to be remembered that during this experiment there were no intervals of darkness. Therefore dark reactions which might occur under normal day-night cycles were eliminated (Lappin 1971, 145).When samples were treated with inhibitors in the case of madder there were some striking results observed, as all inhibitors work very satisfactorily but with all the other dyes used, instability was noticed. As Lappin (1971) states in his earlier study on UV absorbers, the lack of dark intervals in the experimental procedure does not show an accurate imitation of what is happening in the outdoor life and additives may appear to be either more or less stable because of this. As a general observation, hindered amines chosen for this experiment, Tinuvin 770 and Chimassorb 944 show the better results and more stable performance with all treated samples dyed with different dyes and dye combinations and this is also endorsed by de la Rie (1987) in his study of the hindered amines as protective coatings for

paintings. This experimental fact needs more investigation and it would be useful if the selected inhibitors were tested under actual museum conditions for the cycle of a whole calendar year.

It has to be noted here that in all four light fading tests performed in this research, artificial light imitating the sunlight passing through a window glass was used and UV was included. This was because the tests were based on international standards used in industrial testing but also because the use of photodegradation inhibitors in conservation is necessary in non ideal museum conditions. If all UV is excluded during testing, imitating the model museum conditions, as explained in *chapter 2*, photodegradation inhibitors of the class of UV absorbers need not be considered. The induced photodegradation would be attributed only to visible and infrared light. If infrared is also excluded, as is usually done, only visible light can be considered damaging to the most sensitive textile materials. A relevant study presented by Korenberg (2007) showed that there is actually noticeable colour change on cotton, linen and jute fibres when tested excluding all UV radiation, although there was no negative effect on their mechanical properties. In such case, photodegradation inhibitors belonging to the class of antioxidant may prove more successful.

Following the interesting results of the light fastness test No3 and the hypothesis that environmental humidity plays a role in the performance of the additives, more testing was performed using predefined environmental conditions. The outcome of this test was that the action of photodegradation inhibitors is indeed affected by relative humidity and humidity is an important factor to be considered when a treatment is chosen. In this case too, the more light stable dyes seem to benefit from treatments at low, medium and high humidity levels. All the additives perform better at lower humidity and this can be explained by the performance of the dyestuff itself. As fading is retarded on natural dyes in dry conditions, the action of inhibitors is abetted.

Some of the selected inhibitors fail to provide protection on dyed silks at all three levels of humidity, showing that many other factors are affecting their performance such as the type of radiation, type of dye or temperature which was set at 35ºC, a high level for ideal museum conditions but realistic for summer time in the Mediterranean area. The most successful and stable performance at all humidity levels was given by inhibitor combinations, showing that mixtures of UV absorbers and antioxidants present a synergistic effect in the selected environmental conditions. The most satisfying result may be considered that of inhibitor combinations G and H which seem to present an important improvement of light stability of the dyed silks at high humidity levels (80%RH) which can trouble conservators in museums and touring exhibitions with non controllable environment. This action can be explained by the presence of the antioxidant in the inhibitor mixture which stops or retards the photo-oxidation reactions caused by atmospheric oxygen and moisture and the production of hydrogen peroxide. In the mixture the primary action of the UV absorber is to attenuate the intensity of light which is absorbed by the fibres, and as a result the antioxidant can work more efficiently.

Another important observation derived from this test is that at medium relative humidity (50%RH) none of the selected inhibitors provided noticeable improvement of light fastness on dyed silks, with the exception of the two aforementioned inhibitor combinations (G and H) and only in the case of cochineal dyed samples. The performance of inhibitors is of course evaluated in comparison to the colour changes induced in the non treated sample and as this sample is more light stable under these environmental conditions, the action of photodegradation inhibitors is considered unnecessary or negative. This observation needs more testing to be confirmed, when more stable and controlled museum conditions can be imitated in order to evaluate the action of the two successful inhibitor combinations.

In all four tests, almost every additive acts differently with every dye and dye combination and their effectiveness fluctuates from very good to no protection at all. This leads to the

conclusion that much consideration must be given on the identification of dyestuffs present on an historic silk textile, before choosing a treatment. This is also the general outcome of other research done on dyed textiles, which showed that interactions between the inhibitors, fibres, dyes, dye combinations and finishes are very complex (Crews 1984, Thorson 1990). Also it must be taken into consideration that although UV absorbers proved to be effective in retarding yellowing of non dyed fabrics (wool) tested under UV radiation, they seem to be less effective and unstable when sunlight or sources imitating the sunlight are used, as happened in this study (Waters *el al* 1980, 197). Only inhibitor H, which is a combination of a benzotriazole absorber and a hindered amine antioxidant, showed beneficial results in almost every dye and dye combination, although its efficiency is not the same for every case. This observation reinforces the suggestion that there is a synergetic effect between these two inhibitors and its effects are better than each of the two additives alone and far more stable in different dyes and dye combinations used in this study. The best performance of this inhibitor combination was observed in the second light fastness tests when the samples were gradually exposed over different time periods. Inhibitor H not only showed a considerable protection to all dyed samples but it had a stable performance during all time periods as the experiment developed. This observation may be attributed to the fact that there were dark intervals to this experiment. As Shlyapintokh (1983) noticed about synergetic phenomena in polymer photostabilization, when the irradiation is intermittent the synergetic effect is enhanced and this is because the antioxidant is replenished during intervals due to diffusion mechanism. Finally, the positive performance of the same inhibitor combination at different humidity levels warrants more investigation of this rather promising treatment.

11.3 Discussion on Conservation Ethics

Conservation is an action, performed by specially trained staff, that protects objects of archaeological or historical value in such way as to prolong their life as much as possible in order to be enjoyed today and in future generations (Pye 2001, 9). The conservator knows that there is no object kept or displayed in any museum with an infinite lifetime and sometimes there is no point trying to conserve it and as McLeod (1995) said: "nothing is made to last for ever, nothing is made to stay the same during the course of its existence". Only a small amount of objects ever made, finally survived, and are collected, conserved and finally displayed in museums. Most of them were used until worn out, thrown away, reused in another form or simply deteriorated. When an object finally reaches a museum the main hope is nonetheless to make it last "forever" (Bradley 1994) and this heavy duty is usually attributed to the conservator.

Conservators on the other hand, having this huge responsibility on their shoulders, have to follow certain basic ethical rules as far as a treatment is concerned. The first is to question the necessity for any treatment, as the conservator must first clearly understand the existing problem and the necessity and suitability of any intervention. S/he has also to decide the extent of the selected treatment as no treatment should be applied to an object in a more extensive way than necessary (UKIC 1996, 7). The proposal of this research involves the addition of new materials on historic objects and even if they have positive results in photo-protection, the conservator should decide if the particular object every time really needs this kind of protection. This can be achieved through thorough investigation of the problem and risks and the prospective use and environment of the particular object. For example, there is no need of treatment with photodegradation inhibitors to an object which stays in storage most of the time.

It is obvious that not all objects have the same lifetime or reaction to their external environment and this is due primarily to their construction materials. These are the main factors to determine their sensitivity and consequently the conservation treatments selected and applied to

them. Textiles, as already mentioned, are amongst the most fragile objects in a museum collection and their organic nature has the tendency to deteriorate from the very moment of their creation. It is therefore the role of the textile conservator to slow down this procedure by preventive and remedial conservation treatments (Landi 1985, 4).

The conservator, before using any applied treatment, should take into account the available preventive conservation (UKIC 1996, 4) and its limitations. Preventive conservation is understood, and explained in *Chapter 2*, as controlling the environment in storage or display in order to prevent further damage caused by environmental conditions. Textiles benefit from preventive conservation due to their susceptibility to environmental changes and these methods are the first to be considered and applied in any textile collection. On the other hand there are parameters, and one of them is light, that even controlled may cause degradation to most fragile objects and then more interventive methods may be considered.

Remedial conservation, which aims to rectify past degradation, may include treatments that protect objects from further deterioration. There are, for example, remedial treatments that may stabilize the condition of the object. Stabilization is used to stop or retard deterioration with either preventive or interventive techniques (Pye 2001, 30). As the priority of treatment has changed over the years, from the need to make objects look better, if possible like they were new, to the need for methods to make them stable and resistant to further deterioration (Tennent 1992, 166), stabilization methods after basic conservation practices such as cleaning, are strongly considered.

In the terms of stabilization, new mainly synthetic materials are introduced into the object's structure in order to arrest decay or prevent it from reoccurring (Oddy 1994, 4). This may involve materials that are indistinguishable from the original materials, although it is unethical to modify the original nature of the object (Ashley-Smith 1994, 15). In this category falls the use of consolidants in conservation, an action which is very often considered a routine procedure. The

consolidation process involves the introduction of materials into the structure of a deteriorated object by means of impregnation. For example, crumbling stonework, worm-eaten wood, disintegrated archaeological textiles, are consolidated with the introduction of synthetic materials, in an attempt to restore mechanical strength and in a way repair the damage caused by natural processes. Stabilization also includes methods of inhibition of deterioration, again with the addition of materials that have the ability to arrest the causes of certain types of degradation. The photodegradation inhibitors presented in this study belong to this class but perhaps the most famous example is the use of BTA on copper alloy artefacts, although the method is now re-evaluated and many people have given up using it.

Conservation therefore involves making changes to objects, and how intense is this change is determined by several factors such as the condition of the object, the causes of damage but also the future environment and how the object can reciprocate into it (Feilden 1979, 27). There has been a long lasting argument between conservators and conservation scientists but at the end the materials and methods selected should follow the requirements of the objects according to their condition and the dangers they are going to face when displayed in the museum environment (Landi 1985, 4).

With the development of new scientific methods of arresting deterioration or at least retarding it, scientific research should work in collaboration with conservation practices for the well being of the objects. Until the turn of the century, innovations in conservation treatments were made by traditionalist conservators by applying materials and methods to several objects and waiting for the result (Tennent 1992, 165). Many interesting innovations and achievements were made in this way by conservators, resulting in well recognized and successful methods and materials still used today, but many others failed resulting in the destruction of the objects.

Following that, conservation ethics demand that the conservator should never use a treatment or material that will shorten the life of an object, put in danger its original nature,

interfere with future treatment, or avert or obstruct future analysis and research (Ashley- Smith 1994, 15). But how can a conservator ensure all the above when a new treatment is introduced? Conservation science tries to answer the above questions by detailed identification of the problem, by deriving a theoretical solution and finally by practical application and testing (Ward 1986, 33). These tests generally involve artificial aging techniques as the longevity of the materials used is of most interest, and it is important to have the ability to predict their behaviour under extreme conditions (Tennent 1992, 168). The testing of photodegradation inhibitors for textile conservation is at an early stage as there are many questions to be answered and many variables to be taken into consideration before their practical use.

Despite exhaustive aging tests, still some materials have proved to fail long term conservation requirements. This is due to the origin of the objects, their history, their use and their uniqueness that cannot be predicted by controlled accelerated tests. If this is the case, conservators will continue to use methods and materials that they are familiar with and there will be no advancement in the conservation field. As a result, the perfect material for each deterioration problem and for each particular object will never be found and after all, conservation is a compromise. All objects will eventually change and sometimes be lost with the passing of time, and the conservator's role is to work with this change, to investigate it and to control it (Pye 2001, 98).

Under this scheme, the conservator is trying to apply the least possible interventive methods of conservation, not for the beautification of the object, but for its stabilization and prolongation of its life and original looks. To ensure that any treatment applied will not change the appearance, the texture, the material structure or the meaning of the object. This is linked to the preference of selecting conservation materials that can be removed from the object, if this is desirable and possible, without causing further deterioration to the object. As discussed before

(see chapter 5), the reversibility of treatments is not achievable in practice and what is discussed now is the idea of *removability* of the added materials, *retreatability* and minimum intervention.

These notions appear as the more realistic alternatives to reversibility. By the term "removability" it is understood that a material used will have an effect when applied on an object and it will not necessarily disappear after removal. "Retreatability" on the other hand acknowledges that a given treatment will not interfere or obstruct future treatments (Munoz Vinas 2005, 187)

Finally, the conservator's primary intention is to control deterioration of the object by controlling the causes of deterioration (Williams 1997, 199), and performing preventive conservation methods whether an object is stabilized or not.

The above may be confusing and some people tend to believe that in order to have good preservation with permanent results, when valuable objects reach a museum collection, they should never be handled again, and be kept in dark storage rooms with controlled environmental conditions, in organized museums with the appropriate funding. On the contrary the role of the conservator is to find ways to give back the objects to the public in a more stable form and safe environment, as museums are places of research, education and exhibition (Bradley 1994, 54,58).

11.4 Discussion on the use in textile conservation

Summarizing the above mentioned results it can be assumed that photodegradation inhibitors are a promising path for the conservation field and this is the general idea of other research in the field when these materials were tested on picture varnishes and wood finishes (Rene de la Rie 1987, Williams 1983). Although there are some positive results on the improvement of light fastness of naturally dyed textiles in this study, there are many unanswered questions for the use of these materials in the demanding area of textile conservation. Primarily the fact that there is no stable performance of any of the inhibitors selected in this study with all dyes and dye combinations,

opens a whole new world of investigation, as museum textiles consists of a large diversity of construction materials and each one of them should need to be tested with inhibitors and evaluated accordingly. If one imagines that in this study only one parameter was evaluated, such as dye mixtures, the complexity of the situation would be more evident.

Also the method of application and the colour changes investigated on the samples after application are not totally prohibitive for conservation purposes. As Ware introduced in 1994, the perceptible change is expressed by the concept of "just noticeable difference" (JND) and this is a bridge between the scientific approach and a more realistic one. According to science, "any measurable change is damage" while in reality "any change that a human might observe is damage" (Ashley Smith, 1999). According to this, the use of these materials is under consideration when absolutely necessary and there is no other way of protection from light degradation. For example the possible use of the method will find application to remote museums with no available funding for sophisticated pieces of equipment needed for preventive conservation, as well as to objects in loan and touring exhibitions where the lighting conditions can not always predicted.

Removability may be an issue, as it is obvious that the applied inhibitors cannot be completely removed from the silk fabric, but it seems they remain soluble after exposure. It is therefore more important to investigate in depth what is happening during aging of these materials in combination with the textile and its components and to look for any side effects.

Finally much more pragmatic conditions should be used for testing inhibitors for historic silks such as original textile samples and museum environmental conditions. Since UV absorbers for example function primarily with the absorption of UV radiation, what is going to be their performance when ultraviolet light is excluded in the museum environment?

From the above it can be understood that the overall feeling and opinion of the conservators that are possibly going to treat historic textiles with photodegradation inhibitors one

day, is very important. As already mentioned in *chapter* 6 a questionnaire was compiled after the first results of this research.

Fifty copies of the questionnaire were sent to museums that appeared to have textile collections and a conservation or curatorial department. Twenty two of them returned completed and although this means that it is not possible to have a complete picture, a 44% return is a good percentage to attach importance to. A variety of people completed the questionnaire, as was intended, from curators to conservators working in large and well known museums to others occupied in smaller collections. A copy of the questionnaire and a list of people that completed it are given in *Appendix D1,* along with their responsibility and place of work, and I would like to thank them for their interest and collaboration.

The first response of most people who answered the questionnaire, to the idea of using a new material on historic textiles as an interventive method, was negative (10 out of 22), although many of them (13 out of 22) are not satisfied by the performance of preventive conservation methods in their museums, as photodegradation is still observed in their textile objects. At the end of the questionnaire, "no" has become "not yet" as most of them are seeking more information on the subject, the reliability of the testing methods and the accuracy of the results. They would feel more confident if some well known and recognised conservation scientist or laboratory were to propose this treatment[30].

The major concern is the addition of a new material into the textile structure. Although this is not the first time that stabilization remedial treatments are introduced in conservation of cultural heritage, it seems that in the case of textiles which are such vulnerable materials people are much more concerned. Or it is just the case that any new treatment is suspicious until the proof of the contrary?

[30] These conclusions come from extra comments given by people in the questionnaire

Nevertheless, many of the respondents would like to see the performance of photodegradation inhibitors on original historic textile samples as they feel the artificial aging tests are not representative of reality.

The question of reversibility, or rather removability of the inhibitors from the textiles, puzzled all people who responded to this questionnaire. They do not seem to be willing to use the treatment unless they are sure that the new materials can be removed 100% from their textile (18 out of 22). As it was explained in *Chapter 5*, the idea of reversibility of materials used in conservation is simply not realistic and what should be discussed now is the safe removability after aging of the materials. In the present study the attempt of removing inhibitors from fibres after light exposure was promising as it was observed that additives remain soluble after ageing to some extent but still more investigation on the subject will give more accurate answers, probably by using instrumental methods of measuring the extent of removablity of the additives.

Some of the respondents on the questionnaire were more concerned on the long lasting performance of inhibitors when applied to historic textiles and how their presence affects other properties of the textiles, such as flexibility and wash fastness. In the present research this issue was approached partially, as changes of mechanical properties were evaluated only after treatment with inhibitors, but as the fading rate of each sample was evaluated, one has a first idea of the performance of inhibitors through time. As already discussed above, some additives show a better or more stable performance with the passing of time and some exacerbate damage after prolonged exposure. For the best performing additives, one can speculate that either they provide stable protection to textiles through time and this is a desirable result, or the photodegradation process is naturally slowing down after long exposure until no further fading can occur. These questions may be answered with more testing for longer periods and evaluation of the results on fibres and dyes as well as changes on the additives themselves.

Much consideration was also given to the application method used in this research as conservators find it sometimes difficult to use in large textiles, and need special and expensive equipment that not every workshop has available (15 out of 22). This may be confronted using other methods of application such as spraying the solutions of inhibitors to the object's surface and this may be a suggestion of a way of further testing these materials under conservation requirements. Also the health hazards associated with the solvent and the additives have a great effect as, at the end of the day, conservators will be the ones to use them (15 out of 22). The use of alternative solvents or solvent mixtures was also discussed in the present study and surely more experimentation will lead to better solutions. On the other hand, many of the materials and methods used in conservation entail health hazards, such as the extended use of organic solvents and chemicals for cleaning or disinfection and conservators are obliged to protect themselves properly. Nevertheless the approach of minimum intervention to the objects, which is more and more adopted in conservation nowadays, involves less use of materials hazardous to human health.

Finally what was concluded from the questionnaire and the response of conservators to it, is that there is actually a need for more protection for historic textiles rather than the preventive conservation used until now. Historic textiles continue to suffer from photodegradation as long as they are displayed, even in the most large and organized museums. On the other hand we need much more effort and exhaustive testing of new photo-protective materials to satisfy conservation requirements. Much attention must be given not only to the performance of such materials but also to application methods and their practical implementation. For the continuance of any research on the subject, conservators' opinions should be taken into consideration as their suggestions, debate and fears give ideas for more creative research.

12. Recommendations for further research

This study was focused on the evaluation of selected ultraviolet absorbers and antioxidants, for use on historic silks dyed with red natural dyestuffs, in order to increase their light fastness. Since museum textiles have so much complexity, and conservators' problems in this area are quite complicated, there are several recommendations for further research. Some of the following suggestions relate to the methodology of this research and the possible versions that might have been selected if I did the whole thing again from the beginning. Others are suggestions that result from the outcomes of this research, which gave rise to more unanswered questions. Lastly, the suggestions include ideas which are beyond my potential at this stage of work but hopefully will expand research in the field. The recommendations for further research are as follows:

12.1 Repeating particular tests

- ✓ Repeat light fastness test no 4 using all dyed samples and treated with all selected in this research inhibitors and inhibitor combinations, increasing the times of exposure, according to the sensitivity of each dyestuff tested, in all three selected levels of humidity.
- ✓ Use more treated samples (at least 5) for each light fastness test in order to have enough measurements to use for statistical analysis of the results.
- ✓ Repeat mechanical testing of treated samples after light exposure in all three humidity levels, in order to investigate the long term effects on breaking strength and elongation of the fibres treated with inhibitors.

12.2 Selecting testing materials

- ✓ Test the selected photodegradation inhibitors with other natural dyes (such as indigo, fustic, kermes, saffron, weld) and more dye combinations commonly found on historic silks after appropriate identification from original samples.
- ✓ Test the selected inhibitors with more complex samples, such as embroideries or other silk weaves (e.g satin, brocade) that may absorb the inhibitor solution unevenly and have a different performance under light exposure.
- ✓ Test the selected inhibitors on weighted silk with different weighting agents, as it is known that weightings on silk increase its sensitivity to light damage and many historic silks have undergone weighting procedures.
- ✓ Test the selected inhibitors with other types of fibres such as vegetable fibres (cotton and linen) dyed with natural dyes and dye combinations.
- ✓ Test the performance as well as the effects caused by the addition of the selected inhibitors to other materials usually found in historic textiles such as metal threads, paper, leather, glass beads and other organic and inorganic materials.

12.3 Considerations for conservation purposes

- ✓ Since a major problem in conservation is the introduction of a new material into the textile structure, photodegradation inhibitors should be tested on subsidiary materials. There are products in the form of extremely thin and open weaved fabrics that are used in textile conservation as overlays for the stabilization and protection of extremely fragile and fragmented textile objects. These products such as silk and synthetic "crepeline" and "nylon net" are inconspicuous to the human eye and can be dyed in different shades with light fast synthetic dyes. Photodegradation inhibitors can be introduced in this dyeing procedure.

- ✓ To treat dyed samples with photodegradation inhibitors in other solvents and solvent mixtures acceptable in textile conservation that might achieve better surface deposition or infusion of the inhibitors into the fibres.
- ✓ To investigate removability of the additives after ageing not only by light but with other extreme environmental conditions such as high humidity and temperature. Use instrumental techniques to measure the extent of removability of the additives and how this action affects the mechanical and chemical properties of the already degraded fibres.
- ✓ To try methods of application other than immersing the textile in the inhibitor solution, such as spraying the solution onto the fragile fabric surface or gently introducing it with the use of membranes such as Goretex® or Sympatex® used in textile conservation for humidification purposes.

12.4 Testing methodology and selection of additives

- ✓ To test photodegradation inhibitors from the class of excited state quenchers and combine them with UV absorbers and antioxidants in order to investigate if there is a synergetic effect between them and explore the reasons for this synergism. Also experiment with different concentrations and different lighting conditions so as to appraise which mechanism of synergism is effective in each case.
- ✓ To test more commercial products that are water soluble and make comparisons to the solvent soluble ones.
- ✓ To test the most promising additives from the above tests on original historic textile objects. Original historic textiles are already degraded and their degradation products may be catalysts to the photodegradation process.
- ✓ To test the effectiveness of photodegradation inhibitors under specific museum conditions excluding UV light and controlling temperature and relative humidity as ideally is done in a modern museum showcase.

12.5 Research on photodegradation inhibitors and their properties for the needs of conservation science

- ✓ To investigate the degradation mechanism of the photodegradation inhibitors themselves after prolonged exposure to electromagnetic radiation, the possible degradation products they form, and the effect of this mechanism to fibres and natural dyes present on historic textiles.
- ✓ To appraise the maximum time that these additives are beneficial to the textiles without any chemical changes and side effects, calculated under normal museum environmental conditions.
- ✓ Now that conservation requirements are posed on the field, new photodegradation inhibitors may be synthesized accomplishing more of them. For example, inhibitors to be used in conservation do not need to deal so much with ultraviolet light as this can be excluded from museum exhibition or storage areas or they do not need to be insoluble in water or other solvents in order to stay forever, as modern industry requires. On the contrary, they should remain easily soluble even after ageing and they should deal primarily with photodegradation reactions caused by visible light.

13. Conclusions

The present study showed that some commercial photodegradation inhibitors, widely used in the modern polymer industry and successfully tested on several organic polymers, can provide protection from fading of silk fabric dyed with several natural red dyes and dye combinations. Also, a synergetic effect was observed with some inhibitor mixtures providing, in some cases, better photo-stabilization results than each of its components. The methodology of the research was planned with regard to conservation requirements, in order to evaluate these additives as a conservation treatment for historic textiles. The inconsistency of the results, which vary according to the dyes or dye mixtures used, times of exposure and environmental conditions, as well as several unsatisfied points concerning the application of inhibitors to fibres, necessitates further research on the subject. At this stage, the selected photodegradation inhibitors are considered unsuitable for use in textile conservation.

13.1 Considerations on the performance of the additives

The selected photodegradation inhibitors provided some protection from fading of several natural red dyes and dye combinations applied on silk fibres, when exposed to intense lighting, during accelerated tests, imitating sunlight exposure through ordinary window glass. The study therefore showed that additives that have proved successful in modern polymer industry can be considered for other purposes such as conservation of textiles, when other testing criteria are used.

The inhibitors proved to be more effective on the more lightfast dyes, while the light sensitive dyestuffs or dye combinations showed no significant benefit from treatment. The fading rates of the dyed samples during ageing showed that the protection provided by the additives is not stable in all cases and some of the inhibitors lose their effectiveness after prolonged exposure, while others may act as sensitizers with the passing of the time, depending on the dyestuff used. These results indicate the complexity of the situation as far as historic textiles are concerned, and give rise to the differences to be considered, between industrial testing and testing for conservation. It was shown that if one parameter (for example the dye used) is not kept constant, as it is usually done in research for modern applications, the performance of inhibitors is not predictable.

Higher temperature ensures a better environment for the effectiveness of the additives, as at 50°C all inhibitors increased the light fastness of the samples to a certain degree. However, relative humidity also plays an important role and it is concluded that the effectiveness of photodegradation inhibitors is dependent on environmental conditions. More specifically, some of the additives may perform better at low humidity levels (30%RH) which on the other hand are not recommended for textiles. Only one inhibitor combination showed stability in improving the lightfastness of the dyed silks in all three tested humidity levels, although the results given are not all statistically significant. In general the successful inhibitors work satisfactorily on high humidity (80%RH), when fading is accelerated on the non treated sample, while on medium humidity level (50%RH) usually indented for museum environment, they do not seem to add any important benefit to the textiles. Therefore as a conclusion, on ideal and controlled museum environment, the use of photodegradation inhibitors would be unnecessary.

Finally, synergism was observed in mixtures of UV absorbers and antioxidants, with one successful combination showing the most stable performance on certain dyes and dye combinations, especially under controlled environmental conditions. The most successful

additive, inhibitor H, is a mixture of a benzotriazole absorber and a hindered amine antioxidant (inhibitor C and E). This mixture worked better in all four light fastness tests performed in this study, while each of the two components fail to show the same or better results. Still, the results presented by this inhibitor are not in every case statistically significant. Relevant positive results on lower scale though, are also presented by inhibitor G, also a combination of a benzophenone absorber and a hindered amine antioxidant (inhibitors A and D), reinforcing the theory of synergism between additives. It was therefore shown by this study that mixtures of inhibitors showing synergism are the most promising path for conservation research.

13.2 Considerations on use in textile conservation

The photodegradation inhibitors were chosen and tested with regard to conservation requirements and restrictions. This study showed that some commercial additives, commonly used in polymer industry, can satisfy some conservation application requirements and can be considered for further research in the field.

All the selected inhibitors were colourless and applied to the fibres in a solvent, using a technique that simulated dry cleaning in conservation. The colour and the texture of the fibres of the samples were not visibly affected although several, but not significant ,changes in mechanical properties and colour were detected with instrumental methods. The additives remain soluble after application and exposure, and the degree of removability was measured by weight; it was shown that some residues inevitably remained in the textiles. The degree of protection provided by the additives to fibres and dyes is considered significant, but the results vary in every dyed sample. Inhibitors that were successful on one dye were often not successful on another. This means that, in the case of museum historic textiles, where the dye composition may not be known, or where it may vary from one part of the textile to another, it is impossible to select one single treatment with confidence.

The main outcome of this study is that the application of photodegradation inhibitors to historic silk textiles holds promise as a conservation treatment, but needs more research before it can be widely accepted.

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A.1 Sample Information Sheets

Museum	Sample No (Day of Collection)		Sample No (Used in the study)	
Museum of Greek Folk Art	*Front*	*Back*	*Front*	*Back*
Name of Person responsible	1a	1b	1A	1B
P. Kavasila/ E. Karastamati	Colour of the sample		Size of the sample	
Date of sampling	Red		Single Threads	
8/9/1997				

Type of Object	
Shirt Border	
Place of origin	
Island of Crete	
Catalogue No	
50	
Age of the object	
18th century	
Use of the object	
Not often, special occasions like weddings	

Photograph of the object

Methods of handling and treatment during use			
Not known			
Construction technique	Construction Materials		
Embroidery with silk threads on linen background	*Fibres*		*Dyes*
	silk linen		Natural
Date the object came to museum	Importance of object		
1920	very rare		
Date of present display			
1975			
Lighting conditions on display	Conservation applications		
Exclusion of natural light. Artificial light with fluorecence lamps	Wet clanning. Deionized water and Neutralsoap		
Environmental parameters on display	Colourimetric measurements		
Not measured	*1rst*	*2nd*	*3rd*
	Y 4.71	Y 4.92	Y 5.32
Display case	x 0.5115	x 0.5093	x 0.5189
Glass walls with UV filters. Lighting inside display	y 0.3309	y 0.3308	y 0.3312
Support materials for display			
Use of velcro on cotton support. Vertical suspension on plexyglass			

Other comments

The fabrics used are linen and cotton. The stiches employed in Cretan embroideries are the ones used in Byzantine ecclesiastical embroidery. The shades of colour used in the motifs which vary, from a single red or blue colour to multi coloured silks in bright shades, come close to the colour and richness of italian Renaissance silk embroideries.

Museum	Sample No (Day of Collection)		Sample No (Used in the study)	
Museum of Greek Folk Art	*Front*	*Back*	*Front*	*Back*
Name of Person responsible	2a	2b	2A	2B
P. Kavasila/ E. Karastamati	Colour of the sample		Size of the sample	
Date of sampling	Red		Single Threads	
8/9/1997				

Type of Object	
Shirt Border	
Place of origin	
Island of Crete	
Catalogue No	
51	
Age of the object	
18th century	
Use of the object	
Not often, special occasions like weddings	Photograph of the object

Methods of handling and treatment during use			
Not known			
Construction technique	Construction Materials		
Embroidery with silk threads on linen background	*Fibres*		*Dyes*
	silk linen		Natural
Date the object came to museum	Importance of object		
1920	very rare		
Date of present display			
1975			
Lighting conditions on display	Conservation applications		
Exclusion of natural light. Artificial light with fluorecence lamps	Wet cleanning. Deionized water and neutral soap		
Environmental parameters on display	Colourimetric measurements		
Not measured	*1rst*	*2nd*	*3rd*
	Y5.17	Y6.71	Y5.25
Display case	x 0.4784	x 0.4627	x 0.4706
Glass walls with UV filters. Lighting inside display	y 0.2804	y 0.2863	y 0.2836
Support materials for display			
Use of velcro on cotton support. Vertical suspension on plexyglass			

Other comments

The fabrics used are linen and cotton. The stiches employed in Cretan embroideries are the ones used in Byzantine ecclesiastical embroidery. The shades of colour used in the motifs which vary, from a single red or blue colour to multi coloured silks in bright shades, come close to the colour and richness of italian Renaissance silk embroideries.

Museum	Sample No (Day of Collection)		Sample No (Used in the study)	
Museum of Greek Folk Art	*Front*	*Back*	*Front*	*Back*
Name of Person responsible	3a	3b	3A	3B
P. Kavasila/ E. Karastamati	Colour of the sample		Size of the sample	
Date of sampling	Pink		Single Threads	
8/9/1997				
Type of Object				
Bed sheet border				
Place of origin				
Cyclades Islands				
Catalogue No				
643				
Age of the object				
18th century				
Use of the object				
Decorative object. Everyday use				

Photograph of the object

Methods of handling and treatment during use			
Not known			
Construction technique	Construction Materials		
Embroidery with silk threads on linen background	*Fibres*		*Dyes*
	silk linen	cotton	Natural
Date the object came to museum	Importance of object		
1921	very rare		
Date of present display			
1975			
Lighting conditions on display	Conservation applications		
Exclusion of natural light. Artificial light with fluorecence lamps	Wet cleanning. Deionized water and neutral soap		
Environmental parameters on display	Colourimetric measurements		
Not measured	*1rst*	*2nd*	*3rd*
	Y 21.97	Y 25.05	Y 20.84
Display case	x 0.4220	x 0.4182	x 0.4172
Glass walls with UV filters. Lighting inside display	y 0.3230	y 0.3216	y 0.3252
Support materials for display			
Use of velcro on cotton support. Vertical suspension on plexyglass			
Other comments			
Bed sheet border depicting a wedding procession scene on a drawn threadwork ground			

Museum	Sample No (Day of Collection)		Sample No (Used in the study)	
Museum of Greek Folk Art	*Front*	*Back*	*Front*	*Back*
Name of Person responsible	4a	4b	4A	4B
P. Kavasila/ E. Karastamati	Colour of the sample		Size of the sample	
Date of sampling	Red		Single Threads	
8/9/1997				
Type of Object				
Bed Sheet				
Place of origin				
Naxos (cycladic island)				
Catalogue No				
3129				
Age of the object				
18th century				
Use of the object				
Decorative object. Everyday use				

Photograph of the object

Methods of handling and treatment during use			
Not known			
Construction technique	Construction Materials		
Embroidery with silk threads on linen background	*Fibres*		*Dyes*
	silk linen		Natural
Date the object came to museum	Importance of object		
1964	very rare		
Date of present display			
1975			
Lighting conditions on display	Conservation applications		
Exclusion of natural light. Artificial light with fluorecence lamps	Wet cleanning. Support with silk organtine and couching stitch		
Environmental parameters on display	Colourimetric measurements		
Not measured	*1rst*	*2nd*	*3rd*
	Y 5.93	Y 7.63	Y 6.86
Display case	x 0.5106	x. 0.4860	x 0.5086
Glass walls with UV filters. Lighting inside display	y 0.3075	y 0.2987	y 0.3050
Support materials for display			
Use of velcro on cotton support. Vertical suspension on plexyglass			
Other comments Bed spread embroidered all over in red silk thread. Representing a network of stylized leaves.			

Museum	Sample No (Day of Collection)		Sample No (Used in the study)	
Museum of Greek Folk Art	*Front*	*Back*	*Front*	*Back*
Name of Person responsible	_	5	_	5
P. Kavasila/ E. Karastamati	Colour of the sample		Size of the sample	
Date of sampling	Pink		Single Threads	
8/9/1997				
Type of Object				
Towel				
Place of origin				
Cyclades islands				
Catalogue No				
15				
Age of the object				
18th century				
Use of the object				
Often, everyday use				

Photograph of the object

Methods of handling and treatment during use		
Not known		
Construction technique	Construction Materials	
Embroidery with silk threads on linen background	*Fibres*	*Dyes*
	silk linen	Natural
Date the object came to museum	Importance of object	
1919	very rare	
Date of present display		
1975		
Lighting conditions on display	Conservation applications	
Exclusion of natural light. Artificial light with fluorecence lamps	Wet clanning. Deionized water and neutral soap	
Environmental parameters on display	Colourimetric measurements	
Not measured	*1rst*	*2nd*	*3rd*
	Y 25.33	Y 26.43	Y 27.22
Display case	x 0.4305	x 0.4305	x 0.4231
Glass walls with UV filters. Lighting inside display	y 0.3639	y 0.3646	y 0.3685
Support materials for display			
Use of velcro on cotton support. Vertical suspension on plexyglass			

Other comments

The embroideries of the Cyclades (Naxos, Milos, Sifnos, Amorgos) are characterized by their stylized decoration and chromatic unity.

Museum	Sample No (Day of Collection)		Sample No (Used in the study)	
Museum of Greek Folk Art	*Front*	*Back*	*Front*	*Back*
Name of Person responsible	6a	6b	6A	6B
P. Kavasila/ E. Karastamati	Colour of the sample		Size of the sample	
Date of sampling	Orange Red		Single Threads	
9/9/1997				
Type of Object				
Bridal Bed Sheet				
Place of origin				
Epirus - Ioannina				
Catalogue No				
3518				
Age of the object				
18th - 19th century				
Use of the object				
Only used once.				

Photograph of the object

Methods of handling and treatment during use			
Not known			
Construction technique	Construction Materials		
Embroidery with silk threads on linen background	*Fibres*	*Dyes*	
	silk linen	Natural	
Date the object came to museum	Importance of object		
1966	very rare		
Date of present display			
1975			
Lighting conditions on display	Conservation applications		
Exclusion of natural light. Artificial light with fluorecence lamps	Wet clanning. Deionized water and neutral soap		
Environmental parameters on display	Colourimetric measurements		
Not measured	*1rst*	*2nd*	*3rd*
	Y 6.12	Y 7.22	Y 7.76
Display case	x 0.4734	x 0.4889	x 0.4866
Glass walls with UV filters. Lighting inside display	y 0.3587	y 0.3573	y 0.3598
Support materials for display			
Use of velcro on cotton support. Vertical suspension on plexyglass			

Other comments

Bridal bed sheet with dense embroidered ornamentation with the pinecone motif. It is only used once and it was very preciously kept afterwards as it was the evidence of the virginity of the bride.

Museum	Sample No (Day of Collection)		Sample No (Used in the study)	
Museum of Greek Folk Art	*Front*	*Back*	*Front*	*Back*
Name of Person responsible	7a, 7b, 7c	_	7A, 7B, 7C	_
P. Kavasila/ E. Karastamati	Colour of the sample		Size of the sample	
Date of sampling	Orange Red		Single Threads	
9/9/1997				
Type of Object				
Epitaph (Epitafios)				
Place of origin				
Asia Minor				
Catalogue No				
1766				
Age of the object				
1620				
Use of the object				
Used only one month per year				

Photograph of the object

Methods of handling and treatment during use			
Not known			
Construction technique	Construction Materials		
silk satin embroidered with metal and silk threads, lined with a linen plain wave fabric	*Fibres*		*Dyes*
	silk linen	silver threads gold threads	Natural
Date the object came to museum	Importance of object		
1970	very rare		
Date of present display			
1975			
Lighting conditions on display	Conservation applications		
Kept in darkness	Under conservation		
Environmental parameters on display	Colourimetric measurements		
Not on display	7A		
	1rst	*2nd*	*3rd*
Display case	Y 5.76	Y 5.78	Y 6.14
	x 0.3963	x 0.4014	x 0.3929
	y 0.3077	y 0.3062	y 0.3081
Support materials for display	7B		
Not on display	*1rst*	*2nd*	*3rd*
	Y 8.39	Y 11.75	Y 9.69
Other comments	x 0.4438	x 0.3919	x 0.4241
	y 0.3414	y 0.3532	y 0.3501
	7C		
	1rst	*2nd*	*3rd*
	Y 23.15	Y 16.33	Y 11.51
	x 0.3888	x 0.3868	x 03798
	y 0.3799	y 0.3770	y 0.3685

Museum	Sample No (Day of Collection)		Sample No (Used in the study)	
Museum of Greek Folk Art	*Front*	*Back*	*Front*	*Back*
Name of Person responsible	8a	8b	8A	8B
P. Kavasila/ E. Karastamati	Colour of the sample		Size of the sample	
Date of sampling	Red		Single Threads	
10/9/1997				

Type of Object	
Sperveri Door	
Place of origin	
Rhodes island	
Catalogue No	
_	
Age of the object	
18th century	
Use of the object	
Everyday use	Photograph of the object

Methods of handling and treatment during use			
Not known			
Construction technique	Construction Materials		
Embroidery with silk threads on linen background	*Fibres*	*Dyes*	
	silk linen	Natural	
Date the object came to museum	Importance of object		
Not known	Quite rare		
Date of present display			
1975			
Lighting conditions on display	Conservation applications		
Exclusion of natural light. Artificial light with fluorecence lamps	Wet clanning. Deionized water and neutral soap		
Environmental parameters on display	Colourimetric measurements		
Not measured	*1rst*	*2nd*	*3rd*
	Y 7.48	Y 5.93	Y 7.60
Display case	x 0.5079	x 0.5279	x 0.5129
Glass walls with UV filters. Lighting inside display	y 0.3434	y 0.3361	y 0.3453
Support materials for display			
Use of velcro on cotton support. Vertical suspension on plexyglass			

Other comments

Sperveria were long curtains that adorn and isolate the bed from the rest of the house. Their stylized decoration and chromatic unity characteriza the embroideries of the Greek Aegean islands. The entire surface of the tent was embroidered in vertical rows.

Museum	Sample No (Day of Collection)		Sample No (Used in the study)	
Byzantine and Christian Museum	*Front*	*Back*	*Front*	*Back*
Name of Person responsible	_	B	_	9
E. Papastavrou	Colour of the sample		Size of the sample	
Date of sampling	Red		Single Threads	
27/4/1998				
Type of Object				
Ecclesiastical cloth (epigonatio)				
Place of origin				
Florence				
Catalogue No				
T.1024 X.A.E 5002				
Age of the object				
16th century				
Use of the object				
Ecclesiastical often use	Not allowed to take photographs			
Methods of handling and treatment during use				
Not known				
Construction technique	Construction Materials			
Silk satin, painted	*Fibres*		*Dyes*	
	silk		Natural	
Date the object came to museum	Importance of object			
Not known	Rare			
Date of present display				
Not on dislpay				
Lighting conditions on display	Conservation applications			
Kept in darkness Not on display	No conservation			
Environmental parameters on display	Colourimetric measurements			
Not measured	*1rst*	*2nd*	*3rd*	
	Y 7.48	Y 5.93	Y 7.60	
Display case	x 0.5079	x 0.5279	x 0.5129	
Very bad storage conditions	y 0.3434	y 0.3361	y 0.3453	
Support materials for display				
Not on display				

Other comments

It is a sacerdotal vestment, a small rectangular piece of cloth usually hanged from the belt os the archpriest.

Museum	Sample No (Day of Collection)		Sample No (Used in the study)	
Benaki Museum	*Front*	*Back*	*Front*	*Back*
Name of Person responsible	_	M1	_	10
V. Romanou	Colour of the sample		Size of the sample	
Date of sampling	Red		3mm piece of fabric	
28/4/1998				

Type of Object	
Ecclesiastical cloth (epimanikio)	
Place of origin	
Unknown	
Catalogue No	
34218 TA555	
Age of the object	
19th century	
Use of the object	
Ecclesiastical often use	Photograph of the object

Methods of handling and treatment during use			
Not known			
Construction technique	Construction Materials		
Silk satin embroidered with metal threads	*Fibres*		*Dyes*
	silk	Silver Threads Gold threads	Natural
Date the object came to museum	Importance of object		
Not known	Quite important		
Date of present display			
Not on dislpay			
Lighting conditions on display	Conservation applications		
Kept in darkness Not on display	Under conservation		
Environmental parameters on display	Colourimetric measurements		
Not measured	*1rst*	*2nd*	*3rd*
	Y 6.87	Y 6.41	Y 6.64
Display case	x 0.4778	x 0.4718	x 0.4699
Very bad storage conditions	y 0.2844	y 0.2849	y 0.2826
Support materials for display			
Not on display			

Other comments

Epimanikio was the cuff worn by the clerics of the Greek Orthodox Church. Pearls, gold and silver wires are worked with silk thread in a silk ground. The usual subject depicted is that of the Annunciation with the Virgin embroidered on one cuff and the Angel on the other, among floral scrolls.
In this case Christ as the Great Archpriest is depicted

Museum	Sample No (Day of Collection)		Sample No (Used in the study)	
Benaki Museum	*Front*	*Back*	*Front*	*Back*
Name of Person responsible	_	M2	_	11
V. Romanou	Colour of the sample		Size of the sample	
Date of sampling	Red		3mm piece of fabric	
28/4/1998				

Type of Object
Ecclesiastical cloth (epimanikio)
Place of origin
Unknown
Catalogue No
34221, TA 558
Age of the object
19th century
Use of the object
Ecclesiastical often use

Photograph of the object

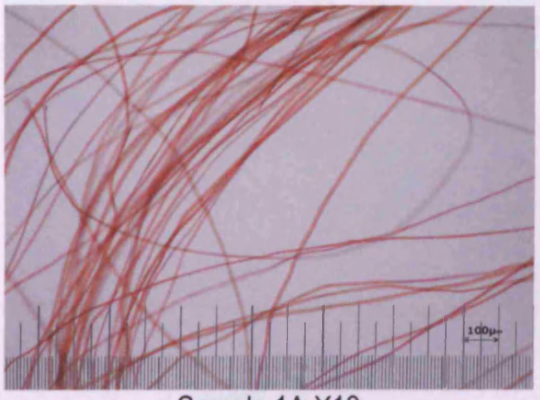
Methods of handling and treatment during use		
Not known		
Construction technique	Construction Materials	
Silk satin embroidered with metal threads	*Fibres*	*Dyes*
	silk silver threads gold threads	Natural
Date the object came to museum	Importance of object	
Not known	Quite important	
Date of present display		
Not on dislpay		
Lighting conditions on display	Conservation applications	
Kept in darkness Not on display	Under conservation	
Environmental parameters on display	Colourimetric measurements	
Not measured	*1rst*	*2nd*	*3rd*
	Y 6.56	Y 4.08	Y 5.71
Display case	x 0.4669	x 0.4372	x 0.4540
Very bad storage conditions	y 0.2977	y 0.2992	y 0.3002
Support materials for display			
Not on display			

Other comments

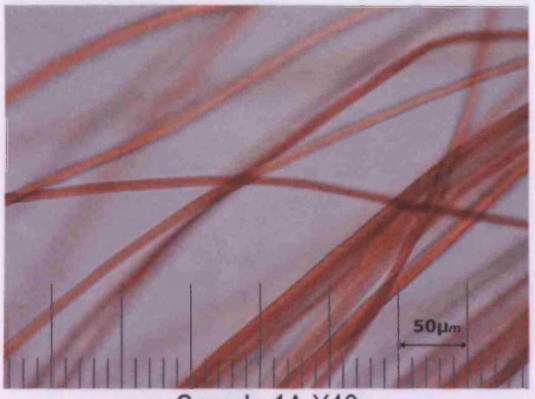
Epimanikio was the cuff worn by the clerics of the Greek Orthodox Church. Pearls, gold and silver wires are worked with silk thread in a silk ground. The usual subject depicted is that of the Annunciation with the Virgin embroidered on one cuff and the Angel on the other, among floral scrolls.
In this case the Virgin with the Child is depicted.

A.2 Microscopic Identification of the Fibres

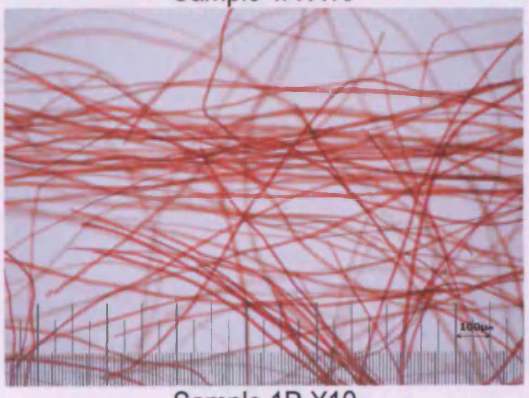
Historic Sample No1



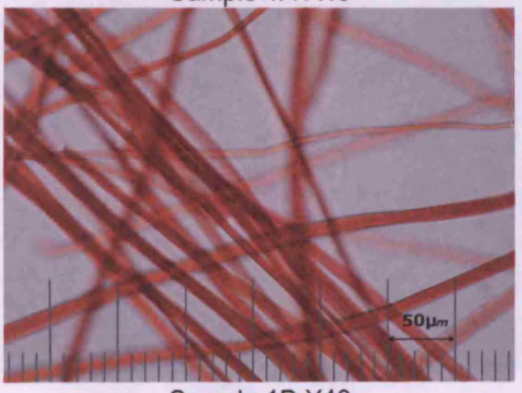
Sample 1A X10



Sample 1A X40

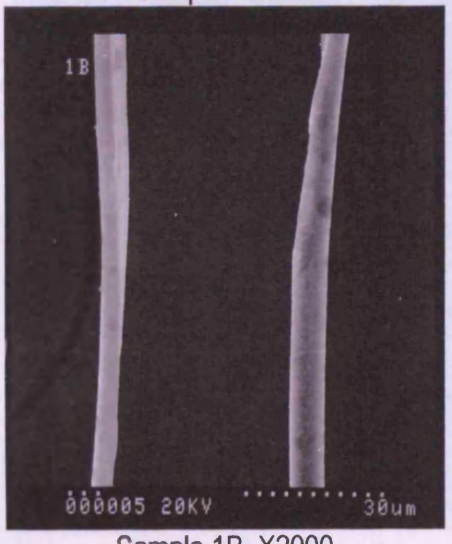


Sample 1B X10



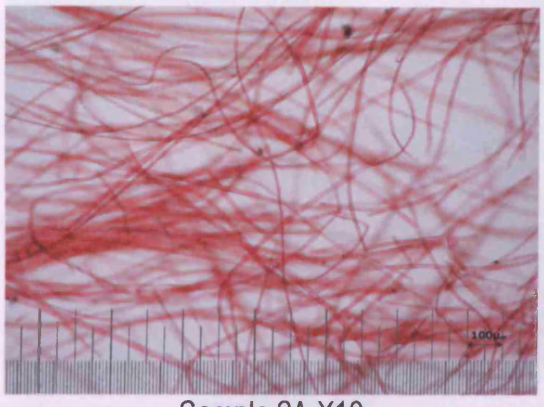
Sample 1B X40

Sample 1A X600

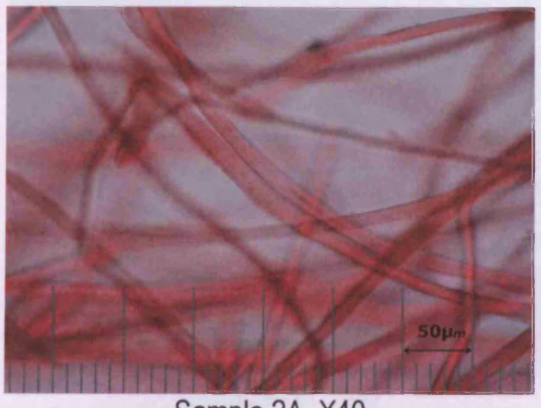


Sample 1B X2000

Historic Sample No2

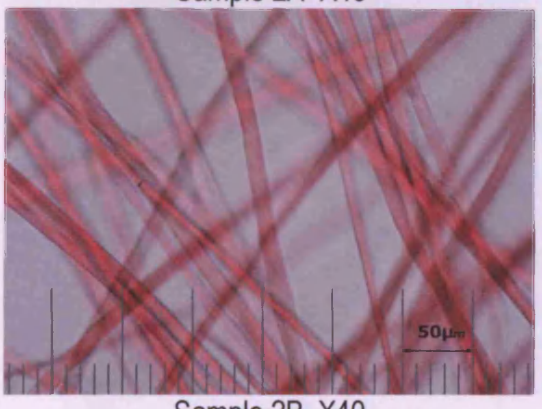


Sample 2A X10

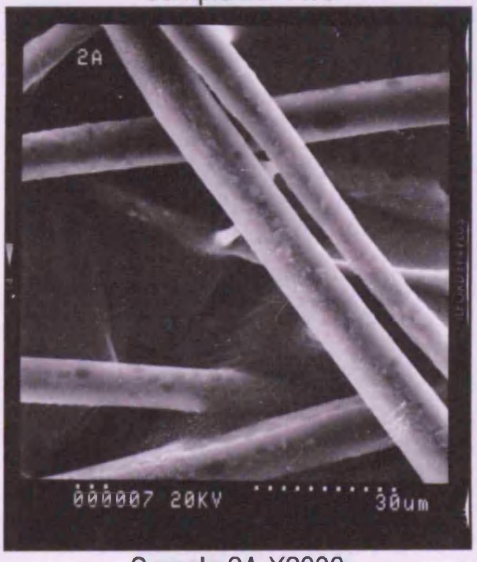


Sample 2A X40

Sample 2B X10



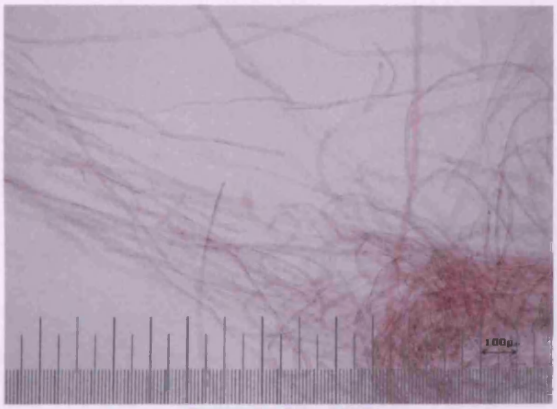
Sample 2B X40



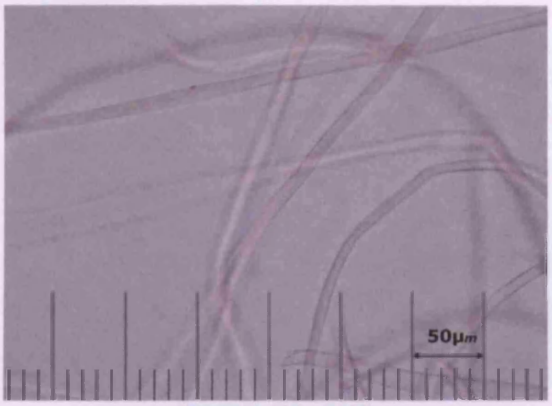
Sample 2A X2000

Sample 2B X500

Historic Sample No3

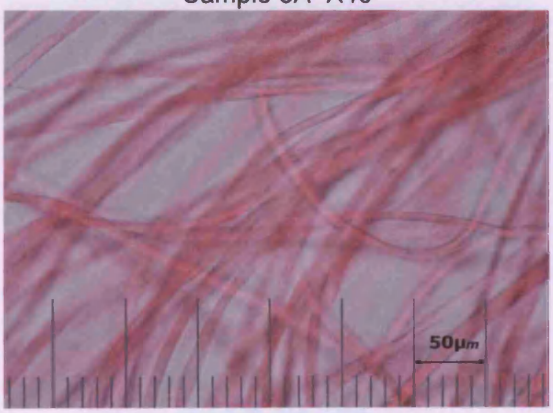


Sample 3A X10

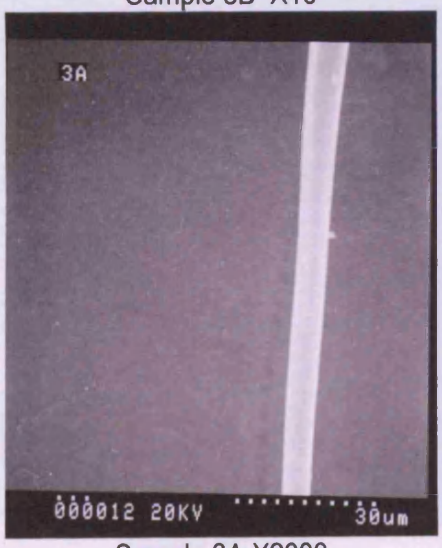


Sample 3A X40

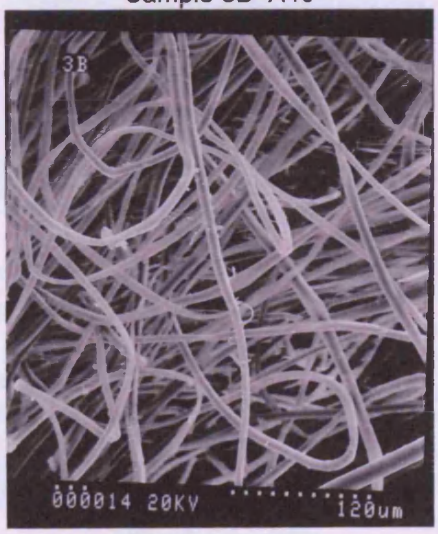
Sample 3B X10



Sample 3B X40



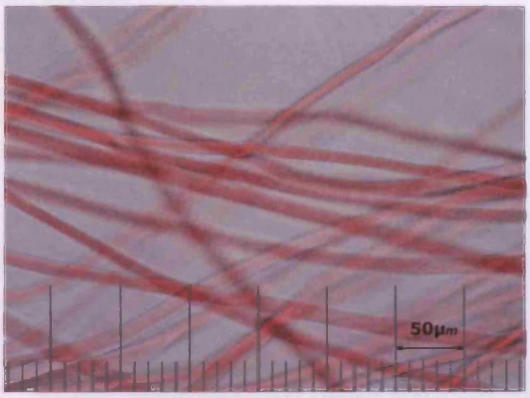
Sample 3A X2000



Sample 3B X500

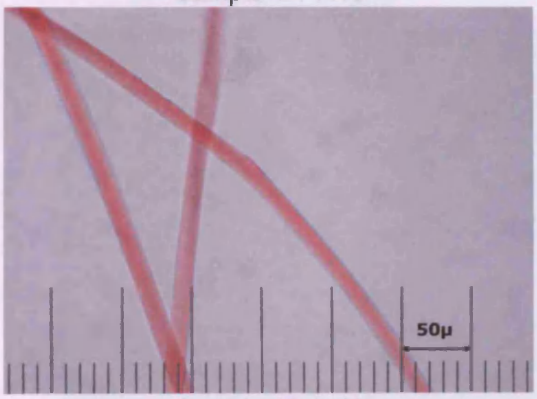
Historic Sample No4

Sample 4A X10

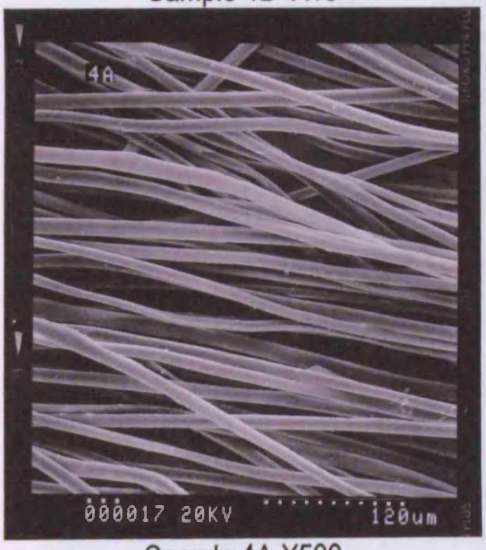


Sample 4A X40

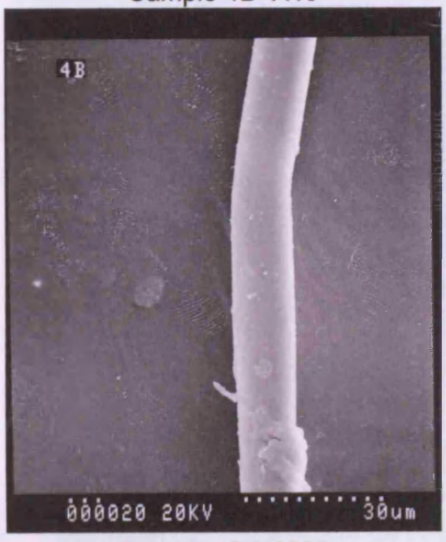
Sample 4B X10



Sample 4B X40



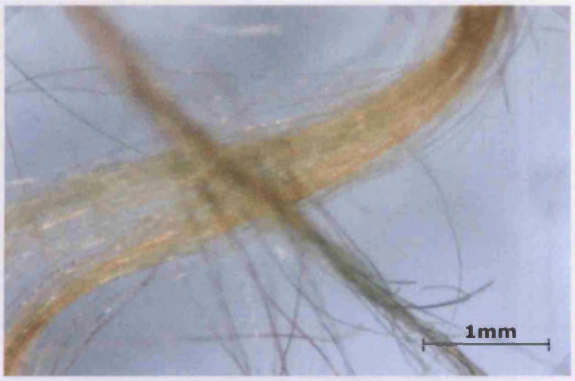
Sample 4A X500



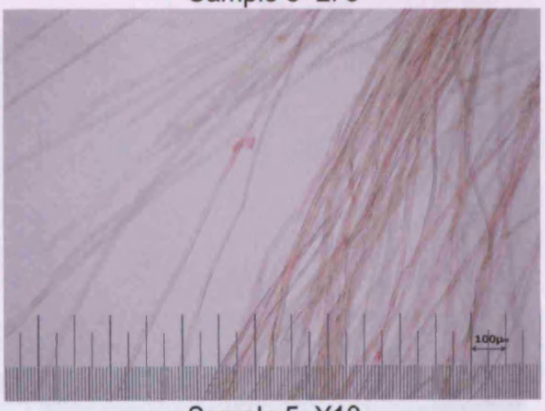
Sample 4B X2000

Historic Sample No5

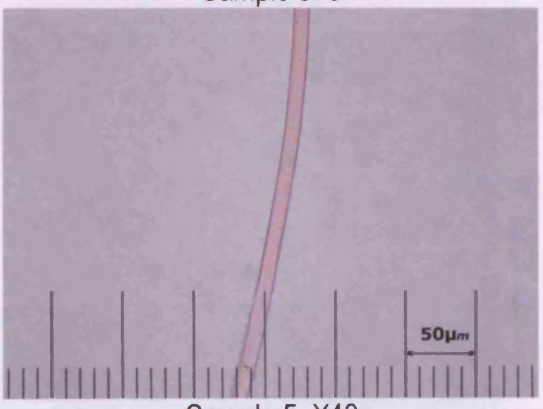
Sample 5×2. 5



Sample 5×5

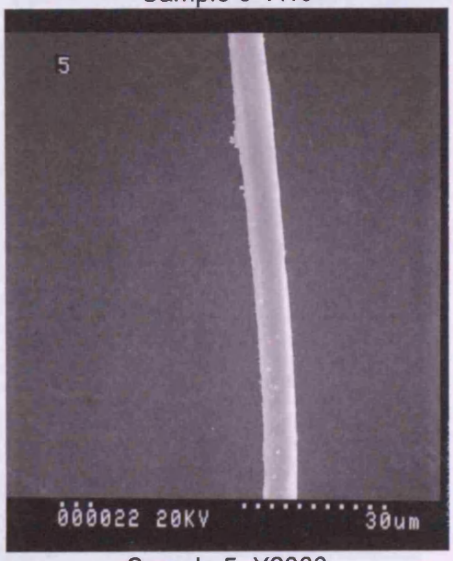


Sample 5 X10



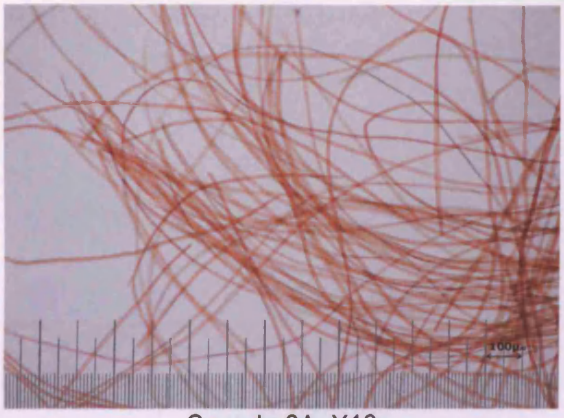
Sample 5 X40

Sample 5 X500

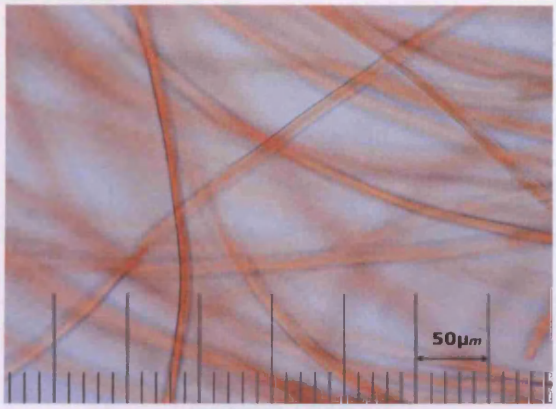


Sample 5 X2000

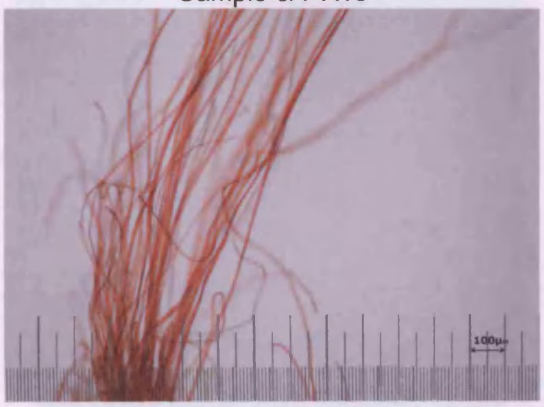
Historic Sample No6



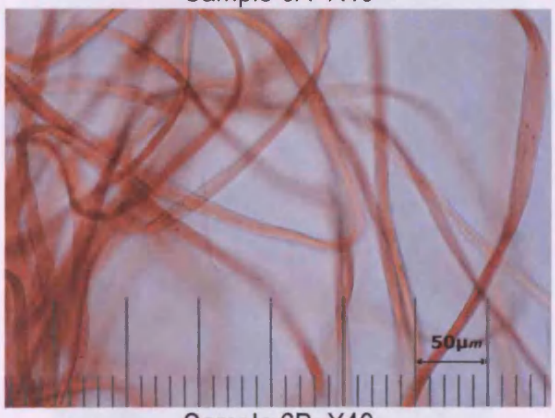
Sample 6A X10



Sample 6A X40

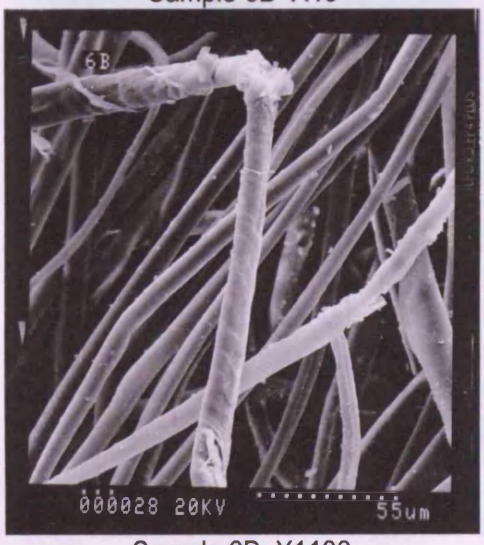


Sample 6B X10



Sample 6B X40

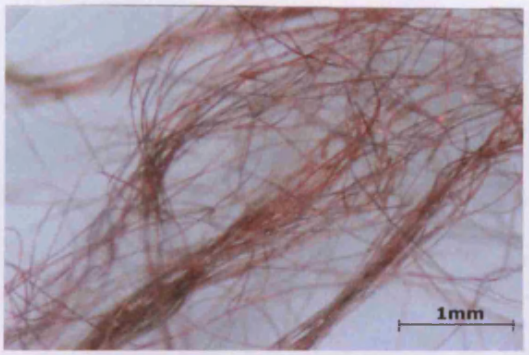
Sample 6B X500



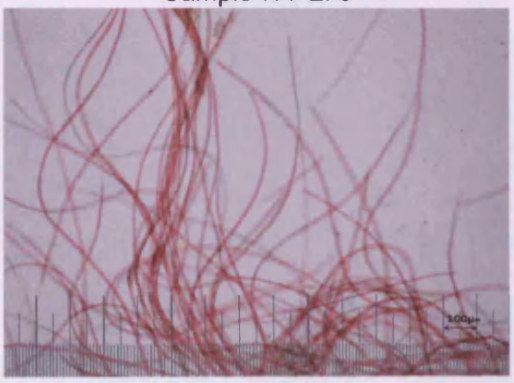
Sample 6B X1100

Historic Sample No7A

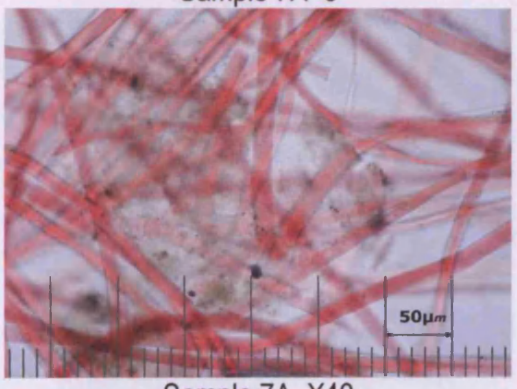
Sample 7A×2. 5



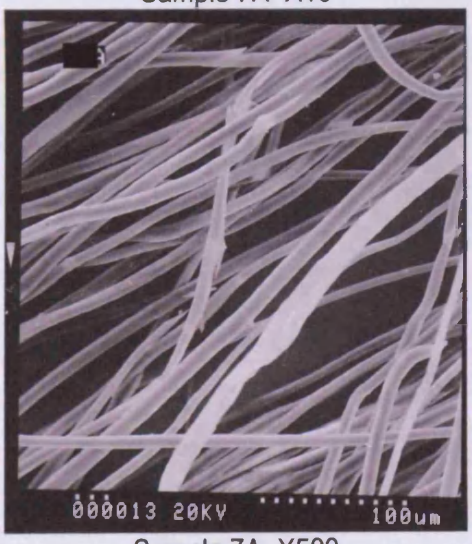
Sample 7A×5



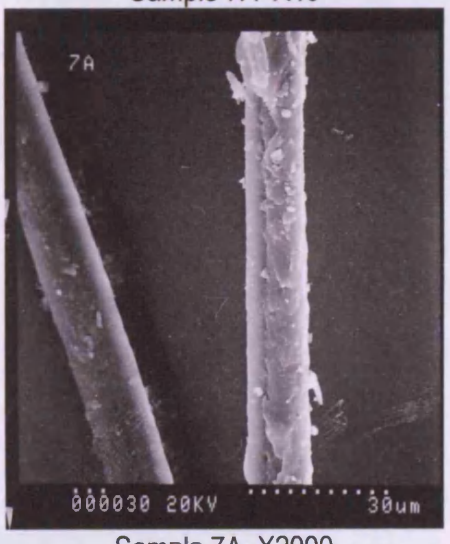
Sample 7A X10



Sample 7A X40



Sample 7A X500

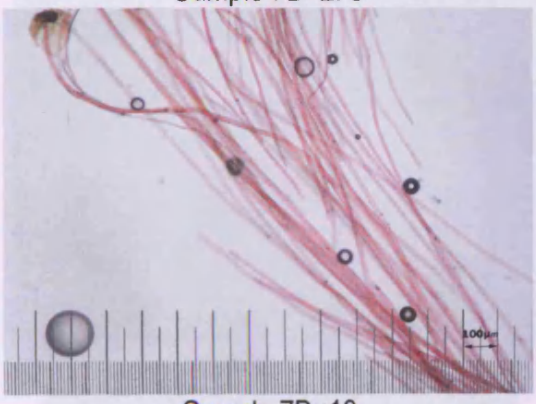


Sample 7A X2000

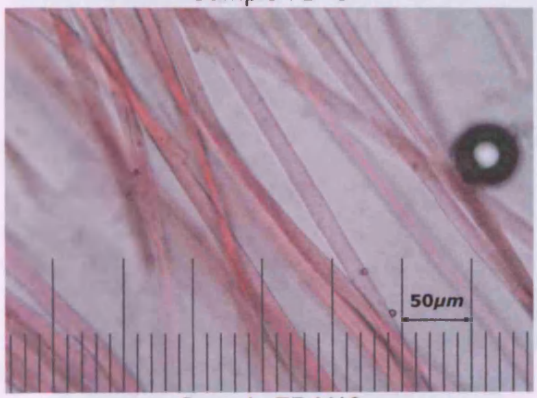
Historic Sample No7B

Sample 7B×2. 5

Sample 7B×5



Sample 7B×10

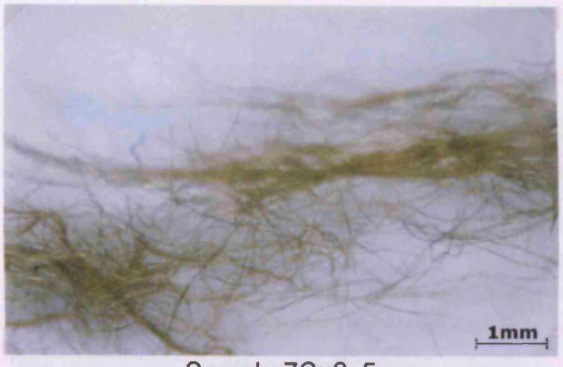


Sample 7B X40

Sample 7B×500

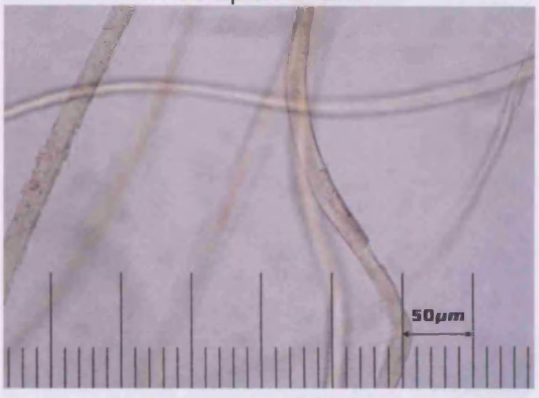
Sample 7B×2000

Historic Sample No7C

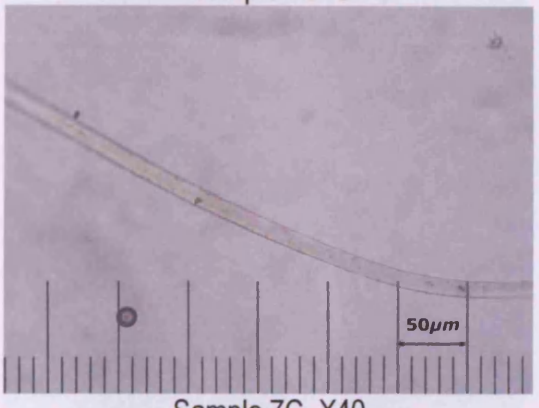


Sample 7C×2. 5

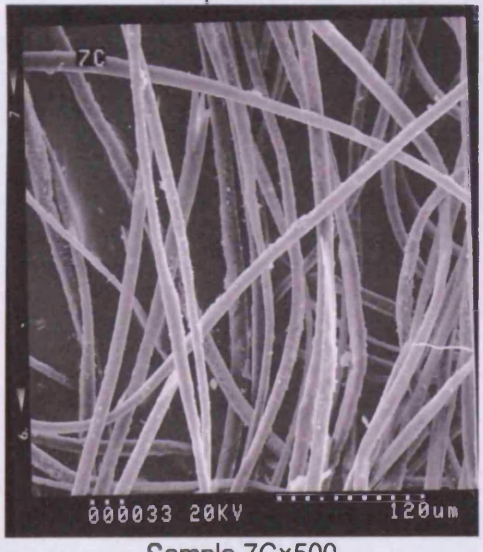
Sample 7C×5



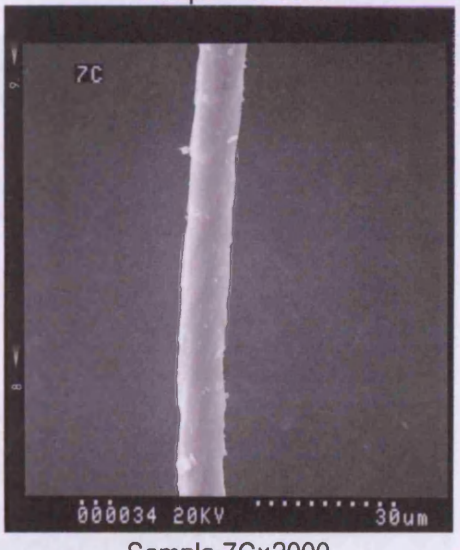
Sample 7C X40



Sample 7C X40



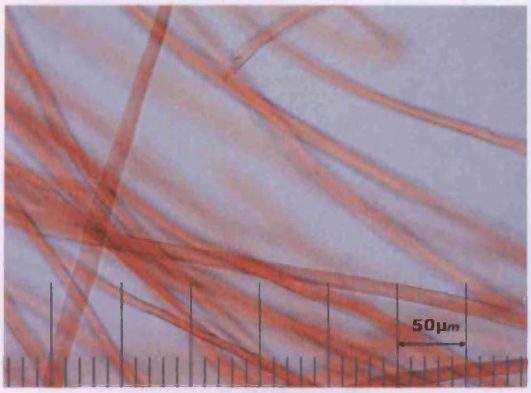
Sample 7C×500



Sample 7C×2000

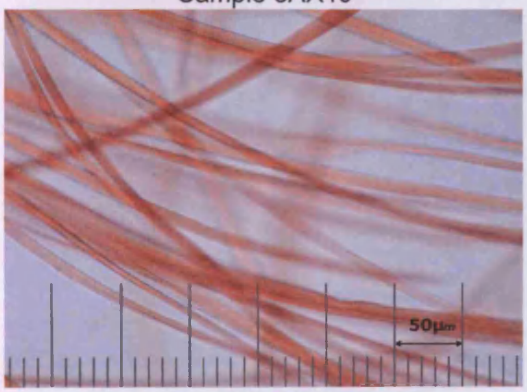
Historic Sample No8

Sample 8AX10

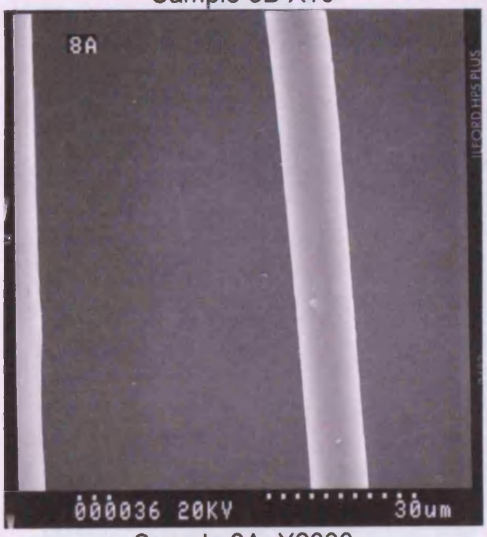


Sample 8AX40

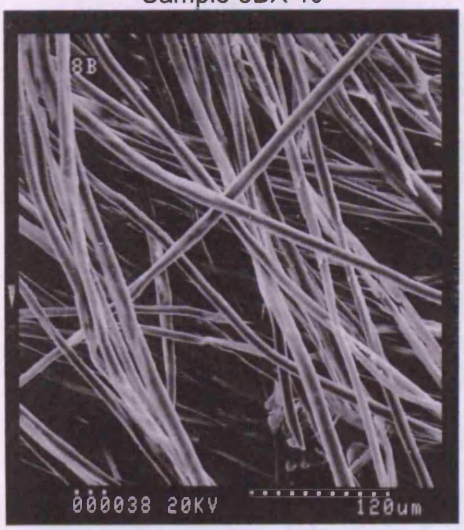
Sample 8B X10



Sample 8BX 40

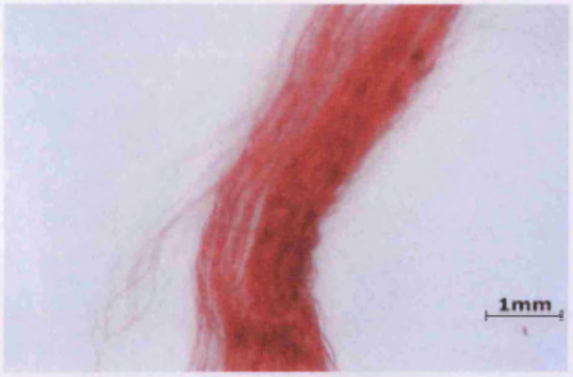


Sample 8A X2000



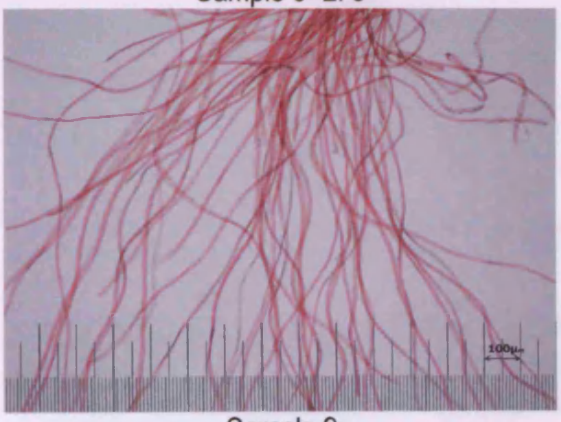
Sample 8B X500

Historic Sample No9

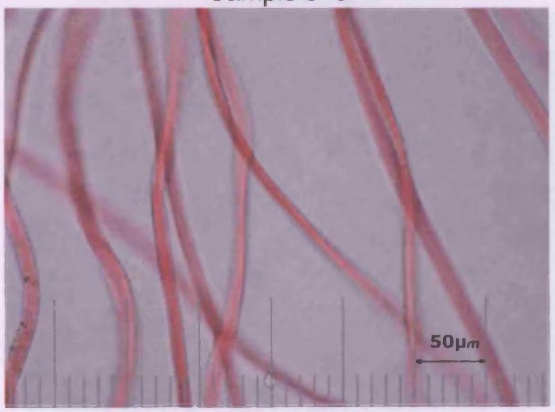


Sample 9×2. 5

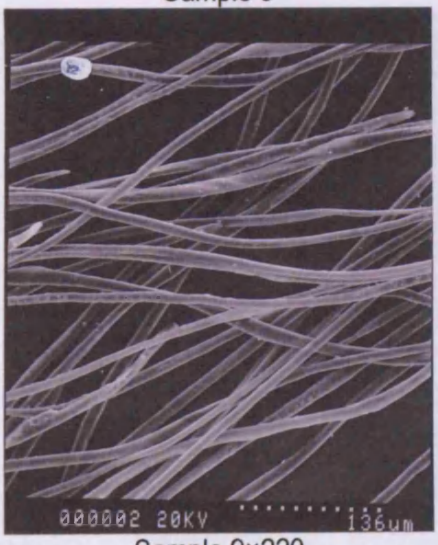
Sample 9×5



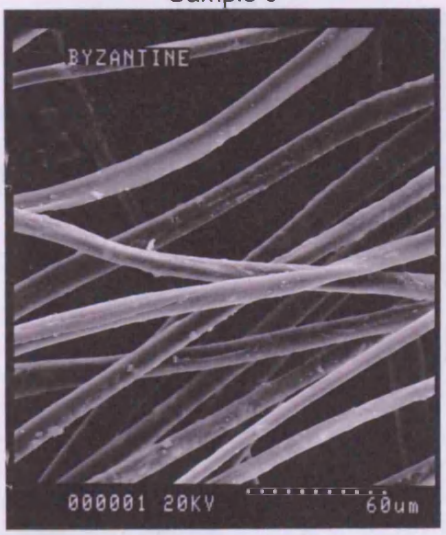
Sample 9



Sample 9



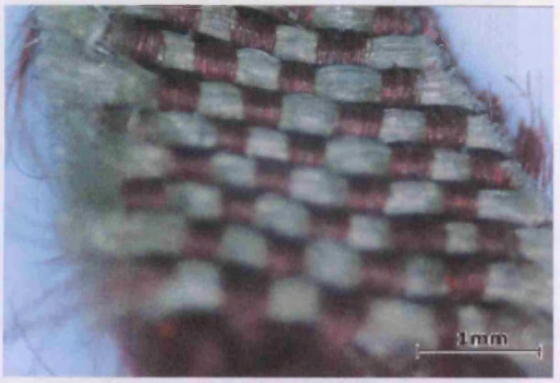
Sample 9×220



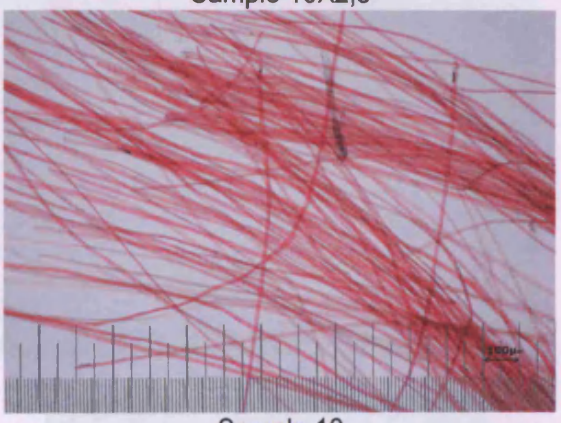
Sample 9×500

Historic Sample No10

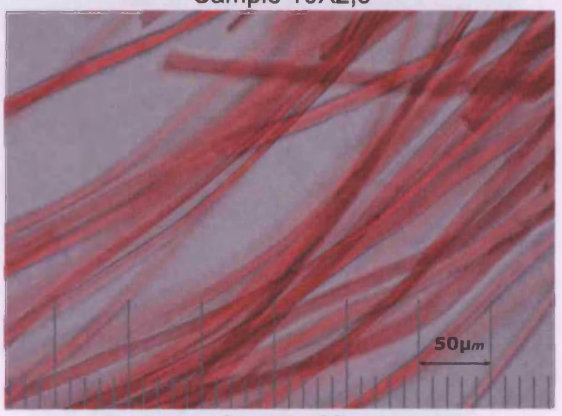
Sample 10X2,5



Sample 10X2,5

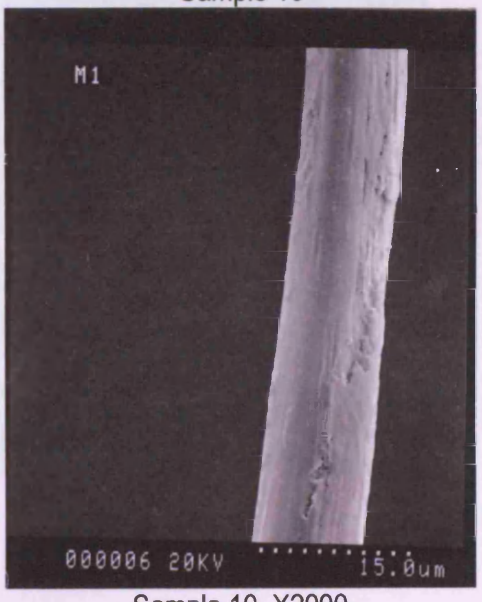


Sample 10



Sample 10

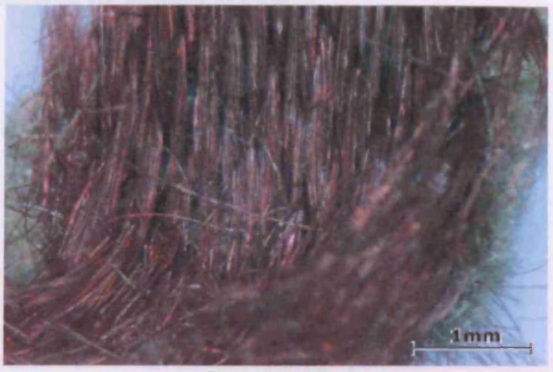
Sample 10 X500



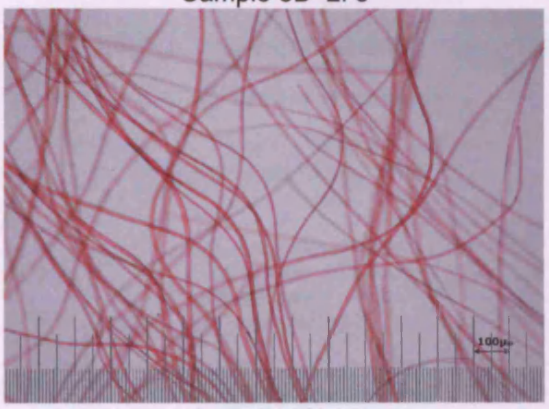
Sample 10 X2000

Historic Sample No11

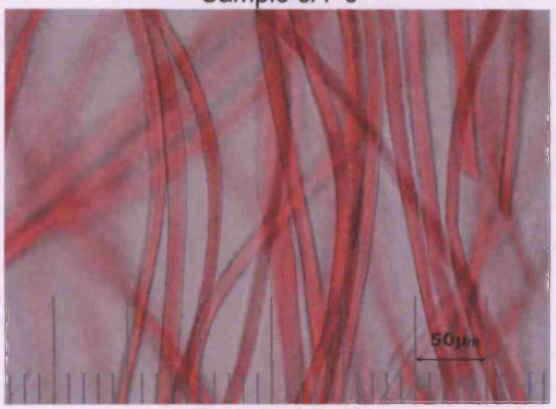
Sample 8B×2. 5



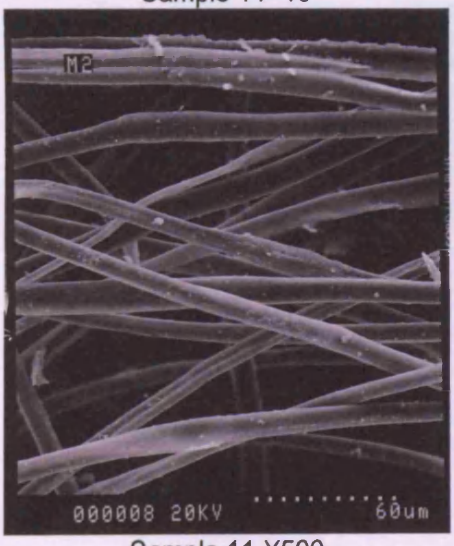
Sample 8A×5



Sample 11×10



Sample 11×40



Sample 11 X500

Sample 11 X2000

A.3 Dye Analysis

A.3.1 Report of the dye analysis of historic samples by Dr.Jan Wouters

KONINKLIJK INSTITUUT VOOR HET KUNSTPATRIMONIUM
Jubelpark 1
B-1000 Brussel
België

Tel. **Fax.** **Email.**

⊃ Bestand : koussoul.001

Brussels, 8 May 1998

Tatiana Koussoulou

Dear Mrs. Koussoulou,

what follows is my report on the dye analyses you requested. I hope you will be satisfied with the results. In the case you would require further informations, please do not hesitate to contact me again.

Best wishes,

Head of Section

1

ANALYSE VAN NATUURLIJKE KLEURSTOFFEN
ANALYSE DE COLORANTS NATURELS

Datum / *Date*	080598
DI / 2L	98 / 6381 2L / 37
Aanvrager / *Demandeur*	Tatiana Koussoulou
Atelier	
Object / *Objet*	Silk
Detail1 / *Détail1*	
Detail2 / *Détail2*	
Detail3 / *Détail3*	
Tijdvak / *Epoque*	18th - 19th Century
Beschaving / *Civilisation*	
Afkomst / *Provenance*	Greece
Plaats / *Lieu*	Museum of Folk Art in Athens
Uitvoerder / *Exécuteur*	

1

CONCLUSION

6381/1: a trace of luteolin (lu) points to the presence of a minor amount of weld (Reseda luteola); a small amount of indigotin (in) indicates the use of an indigoid dye, the exact nature of which cannot be determined as yet (indigo or woad for instance); three components occur with spectral characteristics unknown from our series of reference natural dyes; spectral features and discolouration reactions suggest the presence of a synthetic dye; this would place the dyeing of the fibre in the last quarter of the 19th century or later; a more extensive sampling of this fabric would be advisable.

6381/2: three different sources have been mixed together: a cochineal red, a madder red and tannin. According to the composition of the cochineal red, it is likely that Armenian cochineal (Porphyrophora hamelii) was used. The madder red is Rubia tinctorum. The origin of the tannin cannot be determined because ellagic acid (ea) is formed in all tannin materials upon ageing.

6381/3: all components detected represent safflower (Carthamus tinctorius). The normal colour produced by this source is salmon pink. The presence of yellow "impurities" may modify the hue. This colour is not lightfast. It quickly shifts to light pinkish and beige hues when exposed to light.

6381/4: three different sources have been mixed together: a soluble redwood (orh; a Caesalpinia species), a madder red (Rubia tinctorum) and tannin.

6381/5: three different sources have been mixed together: a soluble redwood (orh; a Caesalpinia species), a madder red (Rubia tinctorum) and tannin. This is the same combination as the one found in 6381/4, but the relative amount of tannin is much higher in the latter.

CODE	CODE KIK / *IRPA*	ANALYSE NR / *NO*	BESCHRIJVING *DESCRIPTION*	SAMENSTELLING *COMPOSITION*	(nm)
sample n°3	6381/1	03/170498/01	pink , Cyclades islands	+ lu, in ?, several components of unknown origin	max
sample n°4	6381/2	04/170498/01	red , Naxos-Cyclades	35.5 ca , 11.5 ea , 1 ag , 1 mu , 35 al , 16 pu , + ru	255
sample n°5	6381/3	05/170498/01	orange , Cyclades islands	13 ct0 , 30 ct1 , 29.5 ct2 , 13 ct3 , 14.5 ap	300
sample n°6	6381/4	06/170498/01	dark red , Epirus , Ioannina	1.5 orh , 29.5 ea , 1 ag , 2.5 mu , 43 al , 22.5 pu	255
sample n°10	6381/5	07/170498/01	red , Rhodes	2 orh , 0.5 ea , 1.5 ag , 2 mu , 60 al , 33.5 pu , 0.5 ru	255

Table of abbreviations

Abbreviation	component (common name) - *source*
ag	anthragallol - *madder red*
al	alizarin - *madder red*
ap	apigenin - *weld, safflower*
ca	carminic acid - *cochineal red*
ctx	unknown - *safflower*
ea	ellagic acid - *tannin*
lu	luteolin - *weld*
mu	munjistin - *madder red*
orh	redwood degradation product - *redwood*
pu	purpurin - *madder red*
ru	rubiadin - *madder red*

Head of Section

ANALYSE VAN NATUURLIJKE KLEURSTOFFEN
ANALYSE DE COLORANTS NATURELS

Datum / *Date*	250698
DI / 2L	98 / 6381 2L / 35
Aanvrager / *Demandeur*	Tatiana Koussoulou
Atelier	
Object / *Objet*	silk
Detail1 / *Détail1*	
Detail2 / *Détail2*	
Detail3 / *Détail3*	
Tijdvak / *Epoque*	16th until 19th century
Beschaving / *Civilisation*	
Afkomst / *Provenance*	Greece
Plaats / *Lieu*	Athens, Museum of Folk Art , Byzantine Museum , Benaki Museum
Uitvoerder / *Exécuteur*	

1

CONCLUSION

6381/6: essentially madder (Rubia tinctorum) with trace of tannin (ea), redwood (orh) and lawson (law)

6381/7: American cochineal (Dactylopius coccus)

6381/8: an insect red, possibly Porphyrophora hamelii (Armenian cochineal), trace of tannin

6381/9: essentially madder (Rubia tinctorum) with trace of tannin (ea) and redwood (orh)

6381/10: essentially redwood (orh) with trace of tannin

6381/11: an insect red, possibly Porphyrophora hamelii (Armenian cochineal), trace of tannin

6381/12: American cochineal (Dactylopius coccus)

6381/13: essentially redwood, small amount of an insect red (species impossible to determine), small amount of tannin, trace of an indigoid dye

6381/14: American cochineal (Dactylopius coccus), small amount of tannin, trace of redwood

The same comments apply as to the first report.

Head of Section

CODE	CODE KIK / *IRPA*	ANALYSE NR / *NO*	BESCHRIJVING *DESCRIPTION*	SAMENSTELLING *COMPOSITION*	(nm)
Sample n°1	6381 / 6	02/260598/01	Red , Greece , 18th century	0.5 law , 0.5 orh , + ea , 1 ag , + ap , 1 mu , 66.5 al , 29.5 pu , 1 ru	255
Sample n°2	3681 / 7	04/260598/01	Red , Greece , 18th century	6.5 dcll , 75.5 ca , 1 orh , 16 ea , 0.5 fk , 0.5 ka , + em <1.3 dcll , 97.5 ca , 0.3 fk , 0.9 ka>	max 275
Sample n°7A	6381 / 8	05/260598/01	Violet red , Asia Minor , 1620	94 ca , 3.5 ea , 1.5 ka , 1 al 99 ca , 1 ka	275 275
Sample n°7B	6381 / 9	06/260598/01	Orange , Asia Minor , 1620	1 orh , 1.5 ea , 1 ag , 2 mu , 63 al , 31.5 pu	255
Sample n°7C	6381 / 10	02/270598/01	Yellow-green , Asia Minor , 1620	81 orh , 19 ea	max
Sample Bz	6381 / 11	03/270598/01	Red , Italy , 16th century	+ dcll, 95.5ca , 3 ea , 0.5 fk , 1 ka + dcll , 98.5 ca , 0.5 fk , 1 ka	275 275
Sample M1	6381 / 12	04/270598/01	Red , 19th century	90 ca , 9.5 ea , 0.5 ka 99 ca , 1 ka	275 275
Sample M1	6381 / 13	05/270598/01	Pink ocre, 19th century	12 ca , 68.5 orh , 18 ea , 1.5 in	255
Sample M2	6381 / 14	06/270598/01	Red , 19th century	83 ca , 1 orh , 15 ea , 0.5 fk , 0.5 ka <2.9 dcll , 98.3 ca , 0.4 fk , 0.7 ka>	max 275

The old technology used for the production of objects of art may be revealed by actual chemical analysis. This is also true for the dyes used for the production of multi-coloured textiles. Since the pioneering work of Pfister (1930-1950) on the systematic chemical analysis of natural dyes from old textiles, much progress has been made in the technology of appropriate analytical techniques. More and more is felt, and also acknowledged, the need to describe an old dyeing into the smallest possible detail, not only to make distinctions between chemically very closely related species, but also to evaluate analytical tolerances determined by crop quality, extraction procedure, dyeing method and ageing phenomena.
The ultimate goal of any dye analysis should be the identification of the biological source(s) used originally for the production of a colour, of which we can only observe the actual hue. Sometimes can be given specific answers to single observations such as the presence of an unusual colour or a colour change within the yarn. The importance of dye analysis of old textiles increases when it can be performed as a function of historical and/or geographical production, of other technological phenomena such as weaving technique or of stylistic observations.

most natural dyes several components contribute to the formation of colour. Moreover, the chemical nature of the components may be very similar, even when from highly different sources. Indeed, anthraquinones and indigoids do occur as well in plants as in animals.
So, what should be aimed for in natural dye analysis is the separation of all the components that are recovered from the dyed fibre, the characterization of each of these that, according to its spectral data, may contribute to colour, the calculation of the relative proportions of the different dye components in the sample and, finally, the evaluation of the results obtained as a function of laboratory experiments on reference products and dyeings and, eventually, known ageing phenomena of individual components.
A specific geographical area of provenance of the fabrics studied, will always necessitate to survey the biological sources of that particular area, known, cited or supposed to have been used for dyeing. However, any such study should always involve the consideration of possible influences caused by commerce with, at least, neighbouring areas.

The amount of sample to be taken from a textile is considered by both the analyst and the textile curator, as a function of the intensity of colouration and the damage to be brought about by the withdrawal of a yarn. A general guideline for the amount of sample needed for reliable quantitative results, also on difficult samples, comes to about 5 mm of wool and 20 mm of silk, or between 0.5 and 1.0 mg of yarn.
All samples were analyzed by high performance liquid chromatography (HPLC). This technique makes possible the separation, identification and quantitation of each dye component in the sample injected. A sample of yarn was treated in water/methanol/37 % hydrochloric acid (1/1/2, v/v/v) for 10 minutes at 100 °C in open Pyrex tubes. The acid preparations were filtered

to remove particulate matter (Vac-Elut, Analytichem, USA) and the clear filtrates were dried in a vacuum dessicator over NaOH. The dry residues were redissolved in methanol/water (1/1, v/v). 20µl of this solution was injected in the chromatographic apparatus. By following this procedure, all of the liquid extracts are used for analysis, so that no component can be lost by preliminary extractions or purifications.
The HPLC equipment consisted of a high-pressure pump programmable for flow-rate, time periods and composition of the eluting solvents (Model M615 pump, Waters, USA); a column with renewable cartridges of 4.6 x 100 mm of Spherisorb ODS2, 3µm (Alltech, Laarne, Belgium); a photodiode array detector (model 991, Waters, USA); a system for data storage, manipulation, and retrieval (Millennium, Waters, USA)). Three solvents were used: (A) water, (B) methanol, and (C) 5% (w/v) phosphoric acid in water. The elution program was: 60A/30B/10C: 3 minutes; linear gradient to 10A/80B/10C: 26minutes; flow rate: 1,2 ml/minute, creating a system back-pressure of 18 to 24Mpa; the temperature in the chromatography laboratory was stabilized between 20°C and 22°C. Any dye component was identified according to two criteria: the retention time and the UV-VIS spectrum.

3

A.3.2 Report of the dye analysis of the newly prepared samples by Ina Vanden Berghe

Dossier / Project	2007.09299
Date of signing the request	06/12/2006
Requestor 1	Ms Koussoulou Tatiana
Requestor 2	
Subject	
Partial subject	

Date of report	12/03/2007
Coordinator	

Object	Silk habotai fabric and silk embroidery threads, dyed with traditional techniques with red natural dyes and combinations Reference samples, prepared in the lab
Author	
Atelier	
Owner	
Era	
Geographical provenance	
Actual location of conservation	

Sampling by	
Assistant sampling	
Sample preparation	
Analyst	

Objective of the analysis	Organic dye analysis

1. HPLC-PDA analysis

List of the abbreviations of the dye components

ag	anthragallol
al	alizarin
pu	purpurin
ru	rubiadin
xp	xanthopurpurin
ca	carminic acid
ka	kermesic acid
fk	flavokermesic acid
dcII	fk glucoside
orh	unknown component of soluble red wood
bra	brasilein
ea	ellagic acid
mu	munjistin

CODE	Code KIK/*IRPA*	ANALYSIS NR	DESCRIPTION	COMPOSITION	λ(nm)
Sample 1	09299 / 01F	06/070207/01	Madder thread	1 ag, 67 al, 1 xp, 30 pu, 1 ru (+ trace ca)	255
Sample 1	09299 / 01T	05/070207/01	Madder fabric	1 ag, 63 al, 35 pu, 1 ru	255
Sample 2	09299 / 02F	07/080207/01	Brasil wood thread	82 orh+bra (11 al, 7 pu)	255
Sample 2	09299 / 02T	08/080207/01	Brasil wood fabric	91 orh+bra (7 al, 2 pu)	255
Sample 3	09299 / 03F	07/070207/01	Safflower thread	(81 al, 19 pu)	255
Sample 3	09299 / 03T	02/080207/01	Safflower fabric	(83 al, 17 pu)	255
Sample 4	09299 / 04F	09/080207/01	Cochineal thread	ca, ka? No dcII and fk	255
Sample 4	09299 / 04T	10/080207/01	Cochineal fabric	+dcII, 100 ca, +ka, +fk !!!!ka before fk !!!! 0,1 dcII, 99.8 ca, 0.1fk ka	255 275R
Sample 5	09299 / 05F	03/080207/01	Brasil wood +madder +tannin thread	(+ca), 3 ea, 1 ag, 67 al, 0.5 xp, 28 pu, 1 ru	255
Sample 5	09299 / 05T	04/080207/01	Brasil wood +madder +tannin fabric	(1.5 ca), 3 ea, 1 ag, 63 al, +xp, 31 pu	255
Sample 6	09299 / 06F	05/080207/01	Brasil wood +madder +tannin +lawson thread	0.5 ea, 0.5 ag, 71 al, 1 xp, 26 pu, 1 ru	255
Sample 6	09299 / 06T	06/080207/01	Brasil wood +madder +tannin +lawson fabric	1 ea, 1 ag, 64 al, 34 pu	255
Sample 7	09299 / 07F	12/080207/01	Cochineal+brazilwood+tannin thread	2 dcII, 95.5 ca, 2 ea, 0.5 ka, + fk !!!ka before fk!!! 0.2 dcII, 99.4 ca, 0.4 fk ka	255 275R
Sample 7	09299 / 07T	11/080207/01	Cochineal+brazil+tannin fabric	2.5 dcII, 51.5 ca, 46 ea, +ka, + fk 0.6 dcII, 98.6 ca, 0.9 fk ka	255 275R

2. Conclusion

CODE	Code KIK/*IRPA*	ANALYSIS NR	DESCRIPTION	BIOLOGICAL SOURCES
Sample 1	09299 / 01F	06/070207/01	Madder thread	Madder (+trace of cochineal)
Sample 1	09299 / 01T	05/070207/01	Madder fabric	Madder
Sample 2	09299 / 02F	07/080207/01	Brasil wood thread	Brasil wood
Sample 2	09299 / 02T	08/080207/01	Brasil wood fabric	Brasil wood
Sample 3	09299 / 03F	07/070207/01	Safflower thread	No dyes detected
Sample 3	09299 / 03T	02/080207/01	Safflower fabric	No dyes detected
Sample 4	09299 / 04F	09/080207/01	Cochineal thread	Cochineal
Sample 4	09299 / 04T	10/080207/01	Cochineal fabric	Cochineal
Sample 5	09299 / 05F	03/080207/01	Brasil wood + madder + tannin thread	Madder and tannin (+trace of cochineal)
Sample 5	09299 / 05T	04/080207/01	Brasil wood + madder + tannin fabric	Madder and tannin (+trace of cochineal)
Sample 6	09299 / 06F	05/080207/01	Brasil wood + madder + tannin + lawson thread	Madder and trace of tannin
Sample 6	09299 / 06T	06/080207/01	Brasilwood + madder + tannin + lawson fabric	Madder and trace of tannin
Sample 7	09299 / 07F	12/080207/01	Cochineal + brasil wood + tannin thread	Cochineal and trace of tannin
Sample 7	09299 / 07T	11/080207/01	Cochineal + brasil wood + tannin fabric	Cochineal and tannin

3. Comment

The identification of safflower is based on the detection of four unidentified, characteristic peaks. None of them was found on the references. Although we have freshly made references where safflower was identified, it is not the first time that the detection of these peaks failed on freshly dyed material.

Neither brasil wood, nor lawson could be identified out of the samples with combinations of red dyes.

In a lot of samples, traces of alizarin and purpurin were found. As they are most probably due to contamination of the column after former, highly concentrated dye samples, they are not considered to be part of the analysis results (and put in between brackets).

However, in case of the traces of carminic acid, found in three of the samples, contamination during the dyeing itself is the most relevant explanation.

Materials and Techniques
KIK

Appendix B – Application of Inhibitors – Evaluation of Treatments

B.1 Inhibitor Absorption

B.1.1 Absorption of photodegradation inhibitors by the silk fabric treated with Acetone solutions

Inhibitors	Treated samples	Before	After	Add on	%abs	Standard deviation
Inhibitor A	A1	0,0985	0,1067	0,008	8,32	*0,63*
	A2	0,1013	0,111	0,010	9,58	
	A3	0,1002	0,109	0,009	8,78	
	Average			0,009	**8,89**	
Inhibitor B	B1	0,0996	0,1097	0,010	10,14	*0,30*
	B2	0,0993	0,1088	0,009	9,57	
	B3	0,0998	0,1098	0,010	10,02	
	Average			0,010	**9,91**	
Inhibitor D	D1	0,1007	0,1106	0,010	9,83	*0,49*
	D2	0,1018	0,1128	0,011	10,81	
	D3	0,103	0,1136	0,011	10,29	
	Average			0,011	**10,31**	
Inhibitor E	E1	0,1036	0,1156	0,012	11,58	*0,70*
	E2	0,1035	0,1155	0,012	11,59	
	E3	0,1016	0,1119	0,010	10,38	
	Average			0,011	**11,19**	
Inhibitor F	F1	0,1	0,1092	0,009	9,20	*0,49*
	F2	0,1025	0,1129	0,010	10,15	
	F3	0,0987	0,108	0,009	9,42	
	Average			0,010	**9,59**	
Inhibitor G	G1	0,1013	0,1103	0,009	8,88	*0,34*
	G2	0,1015	0,1107	0,009	9,06	
	G3	0,1011	0,1096	0,009	8,41	
	Average			0,009	**8,79**	

B.1.2 Absorption of photodegradation inhibitors by the silk fabric treated with Ethanol solutions

Inhibitors	Treated samples	Before	After	Add on	%absorption	Standard deviation
Inhibitor A	A1	0,099	0,106	0,007	7,07	*0,96*
	A2	0,1014	0,1071	0,006	5,62	
	A3	0,1007	0,106	0,005	5,26	
	Average			0,006	**5,99**	
Inhibitor B	B1	0,1018	0,1104	0,009	8,45	*1,22*
	B2	0,1012	0,109	0,008	7,71	
	B3	0,1023	0,1085	0,006	6,06	
	Average			0,008	**7,41**	
Inhibitor D	D1	0,0987	0,1056	0,007	6,99	*0,77*
	D2	0,1028	0,111	0,008	7,98	
	D3	0,1022	0,1088	0,007	6,46	
	Average			0,007	**7,14**	
Inhibitor G	G1	0,1068	0,1149	0,008	7,58	*0,26*
	G2	0,1053	0,1134	0,008	7,69	
	G3	0,1028	0,1111	0,008	8,07	
				0,008	**7,78**	

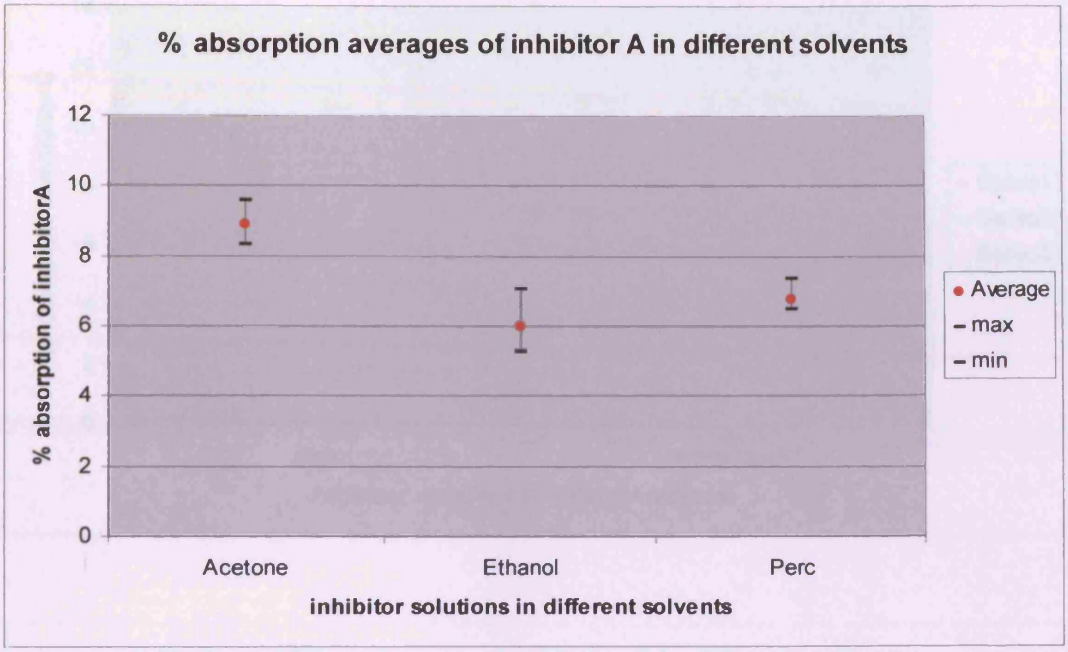
B.1.3 Absorption of photodegradation inhibitors by the silk fabric treated with Tetrachloroetylene solutions

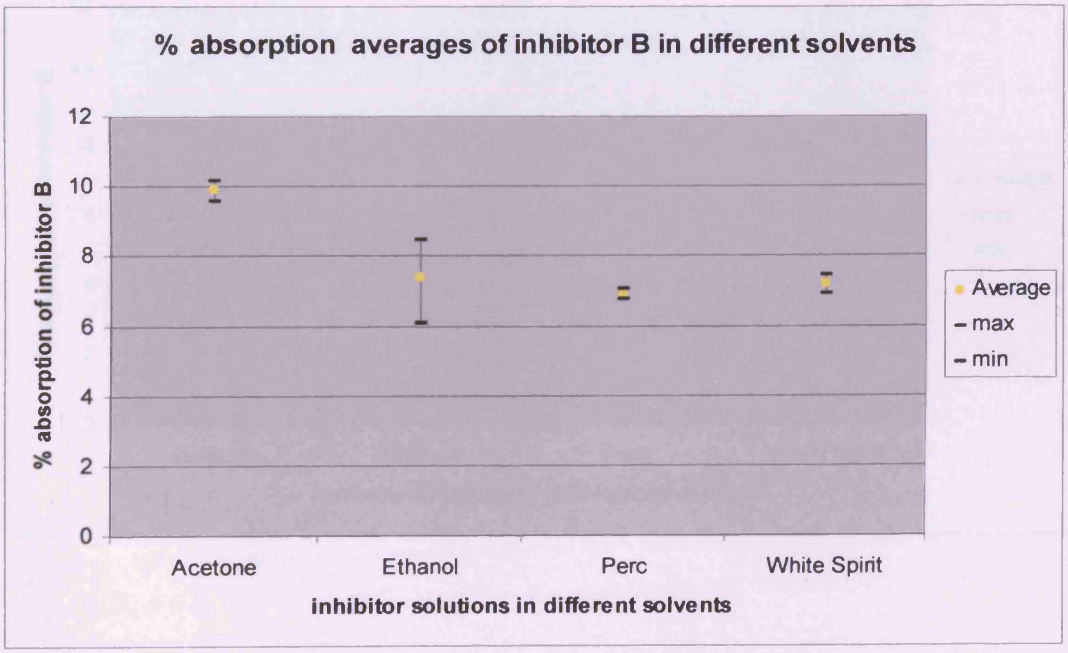
Inhibitors	Treated samples	Before	After	Add on	%absorption	Standard deviation
Inhibitor A	A1	0,0994	0,1067	0,007	7,34	*0,50*
	A2	0,1006	0,1071	0,007	6,46	
	A3	0,0985	0,1049	0,006	6,50	
	Average			0,007	**6,77**	
Inhibitor B	B1	0,1007	0,1078	0,007	7,05	*0,15*
	B2	0,1008	0,1076	0,007	6,75	
	B3	0,1006	0,1075	0,007	6,86	
	Average			0,007	**6,89**	
Inhibitor C	C1	0,1009	0,1086	0,008	7,63	*0,54*
	C2	0,1013	0,1101	0,009	8,69	
	C3	0,1016	0,1097	0,008	7,97	
	Average			0,008	**8,10**	
Inhibitor D	D1	0,1017	0,1115	0,010	9,64	*0,82*
	D2	0,1025	0,112	0,010	9,27	
	D3	0,0992	0,1072	0,008	8,06	
	Average			0,009	**8,99**	
Inhibitor E	E1	0,1005	0,1109	0,010	10,35	*1,36*
	E2	0,1008	0,1138	0,013	12,90	
	E3	0,1001	0,1109	0,011	10,79	
	Average			0,011	**11,34**	
Inhibitor F	F1	0,0989	0,1088	0,010	10,01	*2,83*
	F2	0,1008	0,1159	0,015	14,98	
	F3	0,1013	0,1116	0,010	10,17	
	Average			0,012	**11,72**	
Inhibitor G	G1	0,1013	0,1112	0,010	9,77	*1,44*
	G2	0,0996	0,1065	0,007	6,93	
	G3	0,0997	0,1084	0,009	8,73	
	Average			0,009	**8,48**	
Inhibitor H	H1	0,0993	0,1109	0,012	11,68	*3,95*
	H2	0,0988	0,1115	0,013	12,85	
	H3	0,1009	0,1201	0,019	19,03	
	Average			0,015	**14,52**	
Inhibitor I	I1	0,0991	0,1099	0,011	10,90	*7,26*
	I2	0,1024	0,1129	0,011	10,25	
	I3	0,0994	0,1224	0,023	23,14	
	Average			0,015	**14,76**	

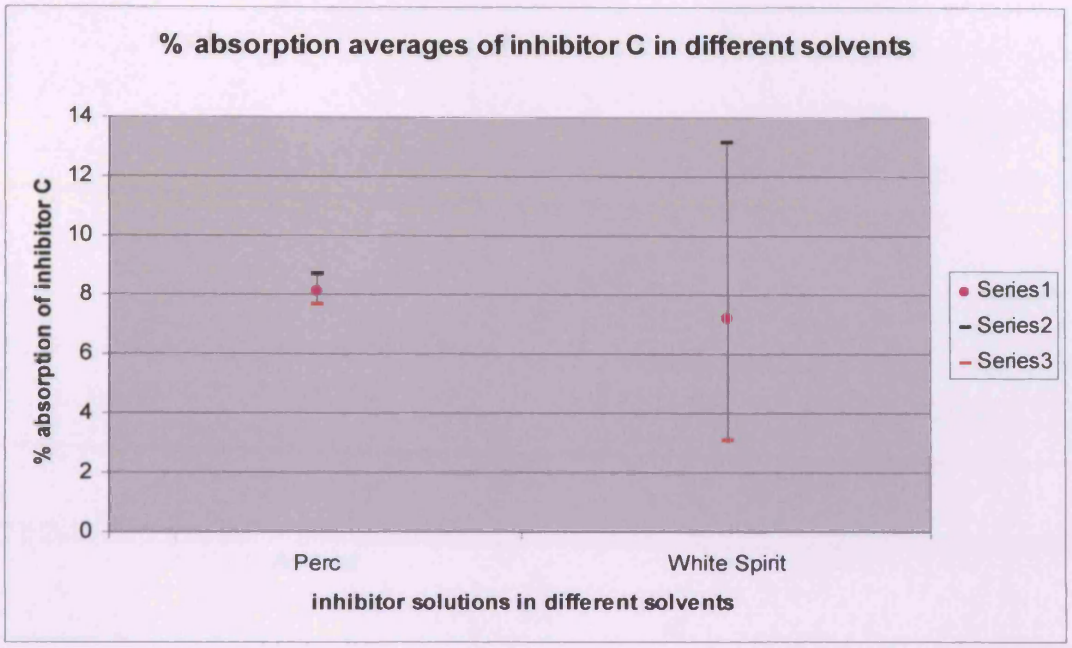
B.1.4 Absorption of photodegradation inhibitors by the silk fabric treated with White Spirit solutions

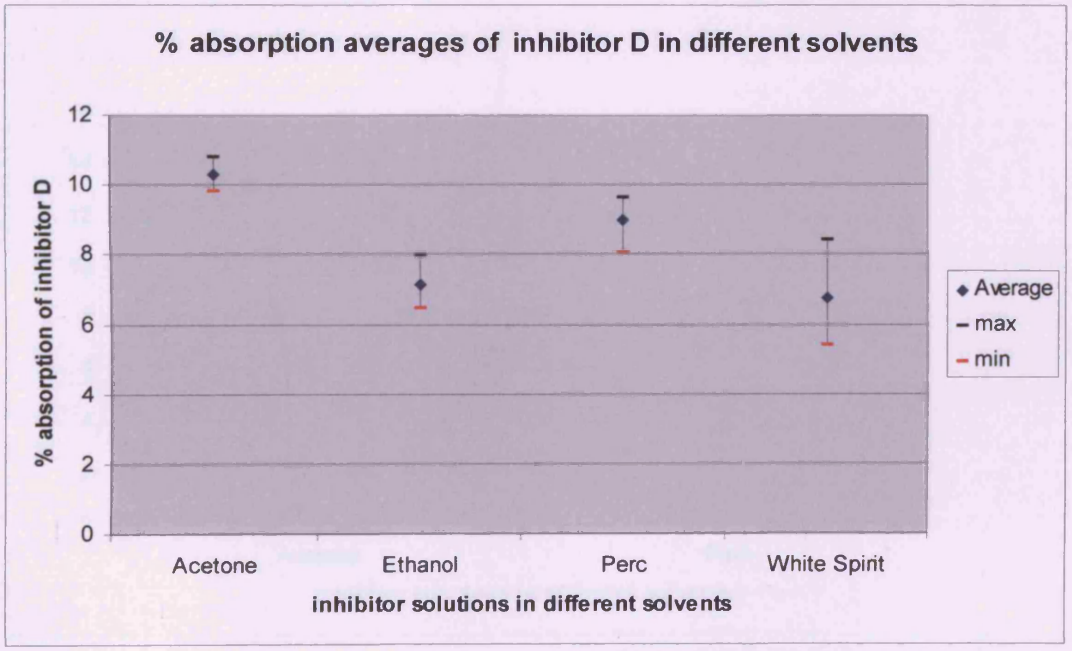
Inhibitors	Treated samples	Before	After	Add on	%absorption	Standard deviation
Inhibitor B	A1	0,0983	0,1054	0,007	7,22	*0,28*
	A2	0,1061	0,1134	0,007	6,88	
	A3	0,0996	0,107	0,007	7,43	
	Average			0,007	**7,18**	
Inhibitor C	B1	0,1014	0,1147	0,013	13,12	*5,25*
	B2	0,0966	0,1019	0,005	5,49	
	B3	0,1012	0,1043	0,003	3,06	
	Average			0,007	**7,22**	
Inhibitor D	D1	0,0997	0,1051	0,005	5,42	*1,53*
	D2	0,1055	0,1123	0,007	6,45	
	D3	0,0986	0,1069	0,008	8,42	
	Average			0,007	**6,76**	
Inhibitor I	G1	0,1017	0,108	0,006	6,19	*1,11*
	G2	0,0994	0,1057	0,006	6,34	
	G3	0,1015	0,1098	0,008	8,18	
	Average			0,007	**6,90**	

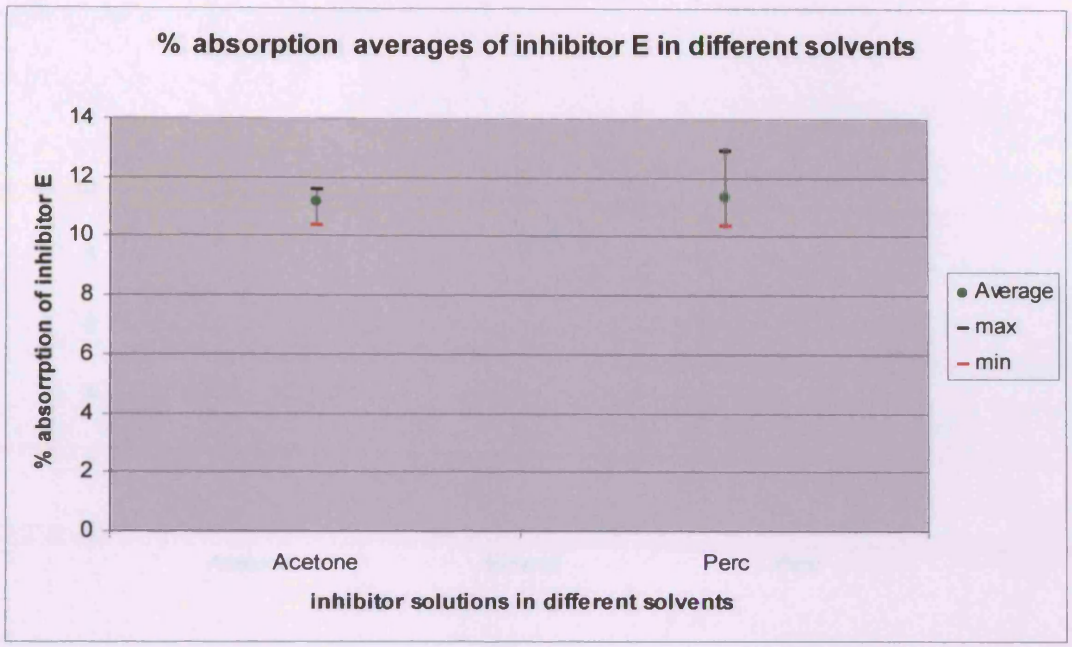
B.1.5 Graphs of % absorption averages of treated with inhibitors silk fabric through different solvent solutions

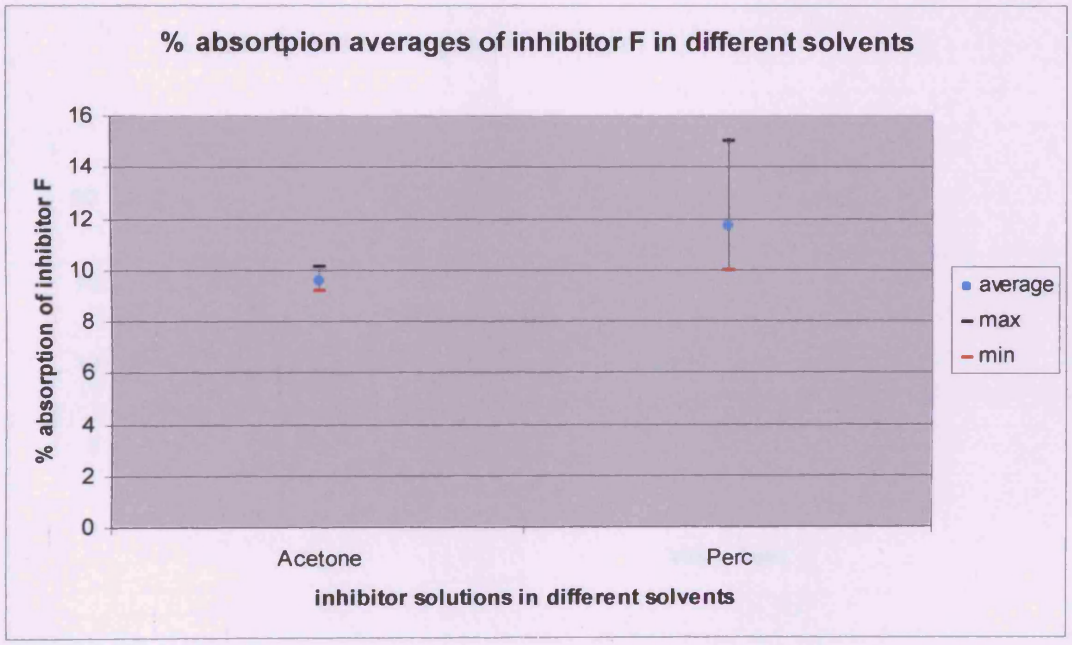


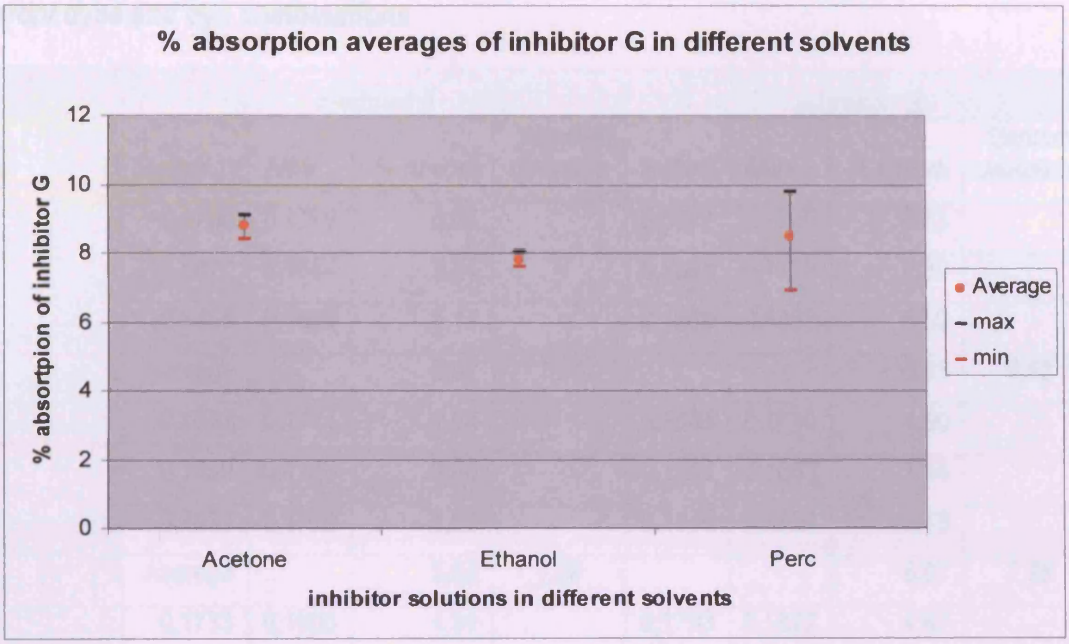


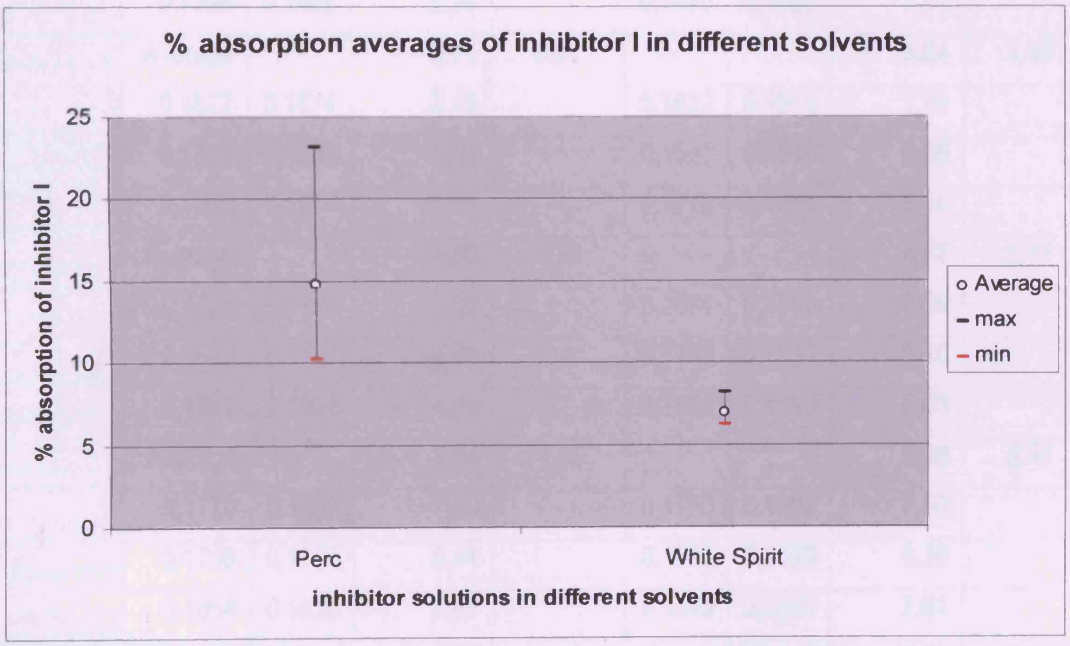

% absorption averages of inhibitor C in different solvents
% absorption of inhibitor C
14
12
10
8
6
4
2
0
Perc
White Spirit
inhibitor solutions in different solvents
Series1
Series2
Series3


% absorption averages of inhibitor D in different solvents
% absorption of inhibitor D
12
10
8
6
4
2
0
Acetone
Ethanol
Perc
White Spirit
inhibitor solutions in different solvents
Average
max
min


% absorption averages of inhibitor E in different solvents
% absorrption of inhibitor E
14
12
10
8
6
4
2
0
Acetone
Perc
inhibitor solutions in different solvents
Average
max
min


% absortpion averages of inhibitor F in different solvents
% absorption of inhibitor F
16
14
12
10
8
6
4
2
0
Acetone
Perc
inhibitor solutions in different solvents
average
max
min


% absorption averages of inhibitor G in different solvents
% absorption of inhibitor G
12
10
8
6
4
2
0
Acetone
Ethanol
Perc
inhibitor solutions in different solvents
Average
max
min


% absorption averages of inhibitor I in different solvents
% absorption of inhibitor I
25
20
15
10
5
0
Perc
White Spirit
inhibitor solutions in different solvents
Average
max
min

B.1.6 Absorption of photodegradation inhibitors by the silk fabric samples dyed with different dyes and dye combinations

	Inhibitor A				Inhibitor B			
Dyes	*Before*	*After*	*% Absorb*	*Standard deviation*	*Before*	*After*	*%Absorb*	*Standard deviation*
Madder	0,1700	0,1789	5,24		0,1677	0,1790	6,73	
	0,1472	0,1587	7,84		0,1657	0,1778	7,30	
	0,1488	0,1565	5,13		0,1568	0,1655	5,50	
	Average		**6,07**	*1,53*			**6,51**	*0,92*
Brazilwood	0,1642	0,1714	4,38		0,1635	0,1713	4,80	
	0,1630	0,1760	8,00		0,1541	0,1663	7,94	
	0,1637	0,1724	5,28		0,1540	0,1624	5,48	
	Average		**5,89**	*1,89*			**6,07**	*1,65*
Safflower	0,1733	0,1808	4,34		0,1793	0,1877	4,67	
	0,1510	0,1586	5,03		0,1501	0,1581	5,34	
	0,1398	0,1482	5,96		0,1470	0,1581	7,51	
	Average		**5,11**	*0,81*			**5,84**	*1,48*
Cochineal	0,1622	0,1674	3,19		0,1622	0,1674	3,19	
	0,1513	0,1582	4,55		0,1521	0,1598	5,05	
	0,1866	0,1974	5,77		0,1772	0,1864	5,18	
	Average		**4,50**	*1,29*			**4,47**	*1,11*
Comb.1	0,1671	0,1790	7,09		0,1671	0,1790	7,09	
	0,1679	0,1757	4,66		0,1759	0,1851	5,20	
	0,1862	0,1952	4,88		0,1883	0,1990	5,68	
	Average		**5,54**	*1,35*			**5,99**	*0,98*
Comb.2	0,1770	0,1902	7,50		0,1770	0,1902	7,50	
	0,1768	0,1864	5,41		0,1585	0,1685	6,30	
	0,1854	0,1925	3,81		0,1470	0,1581	7,51	
	Average		**5,57**	*1,85*			**7,11**	*0,69*
Comb.3	0,1951	0,2043	4,72		0,1951	0,2043	4,72	
	0,2041	0,2141	4,90		0,2110	0,2214	4,92	
	0,1837	0,1939	5,55		0,1878	0,1970	4,89	
	Average		**5,06**	*0,44*			**4,84**	*0,11*

Appendix B: Application of Inhibitors – Evaluation of Treatments

	Inhibitor C				***Inhibitor D***			
Dyes	*Before*	*After*	*%Absorb*	*Standard deviation*	*Before*	*After*	*%Absorb*	*Standard deviation*
Madder	0,1625	0,1716	5,55		0,1745	0,1865	6,88	
	0,1433	0,1547	7,94		0,1622	0,1719	6,01	
	0,1462	0,1540	5,35		0,1479	0,1560	5,46	
	Average		**6,28**	*1,44*			**6,12**	*0,72*
Brazilwood	0,1573	0,1629	3,54		0,1671	0,1749	4,69	
	0,1455	0,1545	6,16		0,1480	0,1596	7,88	
	0,1448	0,1529	5,59		0,1720	0,1816	5,61	
	Average		**5,10**	*1,38*			**6,06**	*1,64*
Safflower	0,1781	0,1855	4,18		0,1720	0,1798	4,54	
	0,1507	0,1529	1,47		0,1546	0,1627	5,23	
	0,1451	0,1536	5,90		0,1499	0,1581	5,52	
	Average		**3,85**	*2,23*			**5,10**	*0,51*
Cochineal	0,1571	0,1629	3,67		0,1598	0,1661	3,92	
	0,1667	0,1758	5,49		0,1613	0,1700	5,36	
	0,1671	0,1765	5,59		0,1783	0,1894	6,24	
	Average		**4,92**	*1,08*			**5,17**	*1,17*
Comb.1	0,1693	0,1801	6,40		0,1695	0,1822	7,52	
	0,1864	0,1964	5,34		0,1774	0,1875	5,72	
	0,1977	0,2079	5,16		0,1771	0,1875	5,89	
	Average		**5,64**	*0,67*			**6,38**	*1,00*
Comb.2	0,1622	0,1734	6,87		0,1677	0,1787	6,59	
	0,2019	0,2148	6,37		0,2014	0,2140	6,25	
	0,1455	0,1545	6,16		0,1499	0,1581	5,52	
	Average		**6,47**	*0,37*			**6,12**	*0,55*
Comb.3	0,2187	0,2282	4,31		0,2006	0,2115	5,42	
	0,2035	0,2132	4,74		0,2230	0,2326	4,30	
	0,1736	0,1831	5,51		0,2047	0,2194	7,16	
	Average		**4,85**	*0,61*			**5,63**	*1,44*

	Inhibitor E				Inhibitor F			
Dyes	*Before*	*After*	*%Absorb*	*Standard deviation*	*Before*	*After*	*%Absorb*	*Standard deviation*
Madder	0,17613	0,18597	5,59		0,16662	0,18387	10,35	
	0,15146	0,16346	7,92		0,14356	0,15633	8,90	
	0,15756	0,17007	7,94		0,14874	0,15945	7,20	
	Average		**7,15**	*1,35*			**8,82**	*1,58*
Brazilwood	0,16642	0,17558	5,50		0,16092	0,17008	5,69	
	0,14873	0,1597	7,38		0,1516	0,1604	5,80	
	0,15249	0,16355	7,25		0,15486	0,16322	5,40	
	Average		**6,71**	*1,05*			**5,63**	*0,21*
Safflower	0,17438	0,18268	4,76		0,17209	0,18116	5,27	
	0,14607	0,1538	5,29		0,14691	0,1561	6,26	
	0,15305	0,16453	7,50		0,1486	0,15872	6,81	
	Average		**5,85**	*1,45*			**6,11**	*0,78*
Cochineal	0,15611	0,16785	7,52		0,16108	0,16789	4,23	
	0,17429	0,18425	5,71		0,16409	0,18004	9,72	
	0,19157	0,20509	7,06		0,18213	0,19154	5,17	
	Average		**6,76**	*0,94*			**6,37**	*2,94*
Comb.1	0,15221	0,18065	18,68		0,16529	0,17912	8,37	
	0,1665	0,17749	6,60		0,1664	0,17335	4,18	
	0,16884	0,17881	5,90		0,16798	0,17877	6,42	
	Average		**10,40**	*7,19*			**6,32**	*2,10*
Comb.2	0,16081	0,17332	7,78		0,17109	0,18439	7,77	
	0,20244	0,21716	7,27		0,20781	0,22213	6,89	
	0,15305	0,16453	7,50		0,17209	0,18116	5,27	
	Average		**7,52**	*0,25*			**6,65**	*1,27*
Comb.3	0,21352	0,22562	5,67		0,21283	0,22408	5,29	
	0,201	0,21178	5,36		0,1939	0,20603	6,26	
	0,19925	0,21142	6,11		0,20207	0,21393	5,87	
	Average		**5,71**	*0,37*			**5,80**	*0,49*

	Inhibitor G				*Inhibitor H*			
Dyes	*Before*	*After*	*% absorb*	*Standard deviation*	*Before*	*After*	*% absorb*	*Standard deviation*
Madder	0,17357	0,1837	5,84		0,17003	0,1822	7,16	
	0,1528	0,16017	4,82		0,15737	0,16632	5,69	
	0,15606	0,16084	3,06		0,16569	0,17777	7,29	
			4,57	*1,40*			**6,71**	*0,89*
Brazilwood	0,15246	0,1604	5,21		0,15868	0,16975	6,98	
	0,1432	0,15253	6,52		0,1423	0,15221	6,96	
	0,15843	0,16875	6,51		0,15963	0,16994	6,46	
			6,08	*0,75*			**6,80**	*0,30*
Safflower	0,17495	0,18298	4,59		0,17345	0,18416	6,17	
	0,15444	0,1627	5,35		0,16999	0,17849	5,00	
	0,15372	0,16318	6,15		0,15489	0,16867	8,90	
			5,36	*0,78*			**6,69**	*2,00*
Cochineal	0,15821	0,16548	4,60		0,15779	0,16661	5,59	
	0,17004	0,17407	2,37		0,17089	0,1813	6,09	
	0,17988	0,19083	6,09		0,1862	0,20029	7,57	
			4,35	*1,87*			**6,42**	*1,03*
Comb.1	0,16339	0,17692	8,28		0,16295	0,17809	9,29	
	0,1825	0,19427	6,45		0,1734	0,18341	5,77	
	0,16463	0,17469	6,11		0,17968	0,19295	7,39	
			6,95	*1,17*			**7,48**	*1,76*
Comb.2	0,1646	0,17537	6,54		0,17662	0,1905	7,86	
	0,19342	0,20489	5,93		0,19765	0,21086	6,68	
	0,15843	0,16875	6,51		0,15489	0,16867	8,90	
			6,33	*0,35*			**7,81**	*1,11*
Comb.3	0,20129	0,21137	5,01		0,19004	0,20052	5,51	
	0,1998	0,21147	5,84		0,2048	0,2169	5,91	
	0,19333	0,20447	5,76		0,19777	0,21223	7,31	
			5,54	*0,46*			**6,24**	*0,94*

	Inhibitor I			
Dyes	*Before*	*After*	*%Absorb*	*Standard deviation*
Madder	0,14779	0,15618	5,68	
	0,14913	0,15649	4,94	
	0,15209	0,16425	8,00	
	Average		**6,20**	*1,60*
Brazilwood	0,1577	0,16719	6,02	
	0,14776	0,15696	6,23	
	0,15925	0,16831	5,69	
	Average		**5,98**	*0,27*
Safflower	0,16729	0,1757	5,03	
	0,17555	0,18412	4,88	
	0,15095	0,15883	5,22	
	Average		**5,04**	*0,17*
Cochineal	0,1470	0,1530	4,09	
	0,17336	0,18386	6,06	
	0,19107	0,2027	6,09	
	Average		**5,41**	*1,15*
Comb.1	0,16505	0,17876	8,31	
	0,1665	0,17653	6,02	
	0,16199	0,17229	6,36	
	Average		**6,90**	*1,23*
Comb.2	0,17857	0,19063	6,75	
	0,17272	0,18281	5,84	
	0,16199	0,17229	6,36	
	Average		**6,32**	*0,46*
Comb.3	0,19672	0,2097	6,60	
	0,2023	0,21104	4,32	
	0,20679	0,22037	6,57	
	Average		**5,83**	*1,31*

B.1.7 Absorption of photodegradation inhibitors by the silk threads dyed with natural dyes and dye combinations

		Inhibitor A				*Inhibitor B*		
Dyes	*Before*	*After*	*%Absorb*	*Standard deviation*	*Before*	*After*	*%Absorb*	*Standard deviation*
Madder	0,04365	0,04865	11,45		0,04238	0,04741	11,87	
	0,04435	0,04952	11,66		0,04296	0,04741	10,36	
	0,04625	0,05258	13,69		0,0421	0,04851	15,23	
	Average		**12,27**	*1,23*			**12,48**	*2,49*
Brazilwood	0,04324	0,04885	12,97		0,04411	0,05	13,35	
	0,041	0,04606	12,34		0,04248	0,04859	14,38	
	0,0467	0,05576	19,40		0,04498	0,05363	19,23	
	Average		**14,91**	*3,91*			**15,66**	*3,14*
Safflower	0,04174	0,04768	14,23		0,04525	0,05141	13,61	
	0,03916	0,04531	15,70		0,04	0,04614	15,35	
	0,04551	0,05209	14,46		0,04587	0,05107	11,34	
	Average		**14,80**	*0,79*			**13,43**	*2,01*
Cochineal	0,04372	0,05095	16,54		0,04135	0,04659	12,67	
	0,04218	0,04719	11,88		0,04356	0,04885	12,14	
	0,0452	0,05033	11,35		0,04265	0,04943	15,90	
	Average		**13,25**	*2,85*			**13,57**	*2,03*
Comb.1	0,04895	0,05444	11,22		0,04734	0,05285	11,64	
	0,04245	0,04857	14,42		0,0428	0,04989	16,57	
	0,04505	0,04993	10,83		0,04374	0,04876	11,48	
	Average		**12,15**	*1,97*			**13,23**	*2,89*
Comb.2	0,04995	0,05521	10,53		0,04776	0,05114	7,08	
	0,04711	0,05243	11,29		0,04591	0,05132	11,78	
	0,04342	0,04892	12,67		0,04242	0,04973	17,23	
	Average		**11,50**	*1,08*			**12,03**	*5,08*
Comb.3	0,04727	0,05387	13,96		0,03115	0,03525	13,16	
	0,03969	0,04728	19,12		0,04144	0,04917	18,65	
	0,04233	0,04797	13,32		0,04028	0,04472	11,02	

	Inhibitor C				***Inhibitor D***			
Dyes	*Before*	*After*	*%Absorb*	*Standard deviation*	*Before*	*After*	*%Absorb*	*Standard deviation*
Madder	0,04575	0,05074	10,91		0,04869	0,05417	11,25	
	0,04604	0,05138	11,60		0,04147	0,04722	13,87	
	0,04569	0,05052	10,57		0,04316	0,04938	14,41	
			11,03	0,52			**13,18**	1,69
Brazilwood	0,04353	0,0501	15,09		0,04363	0,05124	17,44	
	0,04184	0,04758	13,72		0,03778	0,04245	12,36	
	0,04811	0,05484	13,99		0,04422	0,05043	14,04	
			14,27	0,73			**14,62**	2,59
Safflower	0,04115	0,046224	12,33		0,04341	0,04971	14,51	
	0,04026	0,046	14,26		0,04346	0,05006	15,19	
	0,04909	0,05423	10,47		0,0435	0,0492	13,10	
			12,35	1,89			**14,27**	1,06
Cochineal	0,04386	0,0498	13,54		0,04629	0,05128	10,78	
	0,04947	0,05604	13,28		0,04649	0,05432	16,84	
	0,04646	0,0517	11,28		0,047	0,05	6,38	
			12,70	1,24			**11,34**	5,25
Comb.1	0,04614	0,05246	13,70		0,04629	0,05128	10,78	
	0,03994	0,04647	16,35		0,04649	0,05432	16,84	
	0,04604	0,04993	8,45		0,0425	0,04703	10,66	
			12,83	4,02			**12,76**	3,54
Comb.2	0,04914	0,05095	3,68		0,0442	0,04937	11,70	
	0,04575	0,05096	11,39		0,0426	0,0474	11,27	
	0,04873	0,05444	11,72		0,04238	0,04802	13,31	
			8,93	4,55			**12,09**	1,08
Comb.3	0,05084	0,05766	13,41		0,05128	0,05903	15,11	
	0,04367	0,05199	19,05		0,04928	0,05706	15,79	
	0,04437	0,0482	8,63		0,041139	0,0466	13,27	
			13,70	5,22			**14,72**	1,30

Appendix B: Application of Inhibitors – Evaluation of Treatments

	Inhibitor E				Inhibitor F			
Dyes	Before	After	%Absorb	Standard deviation	Before	After	% absorb	Standard deviation
Madder	0,04937	0,05448	10,35		0,04735	0,05226	10,37	
	0,04495	0,04986	10,92		0,04356	0,04868	11,75	
	0,04278	0,04923	15,08		0,04157	0,04751	14,29	
	Average		**12,12**	*2,58*			**12,14**	1,99
Brazilwood	0,04257	0,04947	16,21		0,04432	0,051208	15,54	
	0,04833	0,05592	15,70		0,05019	0,05811	15,78	
	0,04612	0,05508	19,43		0,0434	0,04956	14,19	
	Average		**17,11**	*2,02*			**15,17**	0,86
Safflower	0,04643	0,05499	18,44		0,04317	0,04839	12,09	
	0,04304	0,04973	15,54		0,03905	0,04959	26,99	
	0,0451	0,05196	15,21		0,04848	0,05485	13,14	
	Average		**16,40**	*1,77*			**17,41**	8,32
Cochineal	0,05157	0,06431	24,70		0,04526	0,05152	13,83	
	0,05015	0,05705	13,76		0,04171	0,04699	12,66	
	0,0473	0,05286	11,75		0,0442	0,04956	12,13	
	Average		**16,74**	*6,97*			**12,87**	0,86
Comb.1	0,04612	0,05207	12,90		0,05187	0,05655	9,02	
	0,04963	0,05664	14,12		0,04854	0,05531	13,95	
	0,04393	0,05024	14,36		0,0502	0,05601	11,57	
	Average		**13,80**	*0,78*			**11,51**	2,46
Comb.2	0,04493	0,04948	10,13		0,05258	0,05744	9,24	
	0,04272	0,04926	15,31		0,04327	0,04788	10,65	
	0,0444	0,04926	10,95		0,0447	0,05017	12,24	
	Average		**12,13**	*2,79*			**10,71**	1,50
Comb.3	0,05113	0,05695	11,38		0,02817	0,03219	14,27	
	0,04427	0,05143	16,17		0,0505	0,05761	14,08	
	0,04235	0,04893	15,54		0,0403	0,04568	13,35	
	Average		**14,36**	*2,60*			**13,90**	0,49

	Inhibitor G				***Inhibitor H***			
Dyes	*Before*	*After*	% absorb	Standard deviation	*Before*	*After*	*% absorb*	*Standard deviation*
Madder	0,04458	0,0495	11,04		0,05442	0,06042	11,03	
	0,04238	0,0467	10,19		0,04511	0,05001	10,86	
	0,04832	0,05284	9,35		0,04833	0,05308	9,83	
	Average		**10,19**	*0,84*			**10,57**	*0,65*
Brazilwood	0,04484	0,05168	15,25		0,04738	0,06034	27,35	
	0,04515	0,05427	20,20		0,04313	0,05179	20,08	
	0,04574	0,05134	12,24		0,04738	0,0551	16,29	
	Average		**15,90**	*4,02*			**21,24**	*5,62*
Safflower	0,04763	0,0539	13,16		0,04318	0,05088	17,83	
	0,0412	0,04819	16,97		0,04168	0,04982	19,53	
	0,04494	0,05163	14,89		0,04253	0,04997	17,49	
	Average		**15,01**	*1,90*			**18,29**	*1,09*
Cochineal	0,0484	0,05295	9,40		0,05359	0,06268	16,96	
	0,04288	0,04732	10,35		0,04273	0,04817	12,73	
	0,0449	0,05099	13,56		0,0444	0,04936	11,17	
	Average		**11,11**	*2,18*			**13,62**	*3,00*
Comb.1	0,0489	0,05425	10,94		0,05156	0,05828	13,03	
	0,04242	0,04736	11,65		0,04858	0,05602	15,31	
	0,04735	0,05287	11,66		0,04663	0,05213	11,79	
	Average		**11,41**	*0,41*			**13,38**	*1,79*
Comb.2	0,04789	0,05336	11,42		0,05074	0,05854	15,37	
	0,04649	0,05235	12,60		0,04476	0,05095	13,83	
	0,0432	0,04862	12,55		0,0486	0,05535	13,89	
	Average		**12,19**	*0,67*			**14,36**	*0,87*
Comb.3	0,04812	0,05508	14,46		0,05259	0,06104	16,07	
	0,04837	0,0553	14,33		0,04273	0,05206	21,83	
	0,04622	0,05256	13,72		0,04451	0,05216	17,19	
	Average		**14,17**	*0,40*			**18,36**	*3,06*

	Inhibitor I			
Dyes	*Before*	*After*	*%Absorb*	*Standard deviation*
Madder	0,04543	0,051113	12,51	
	0,04397	0,04865	10,64	
	0,04885	0,05318	8,86	
	Average		**10,67**	*1,82*
Brazilwood	0,04466	0,05203	16,50	
	0,04225	0,05022	18,86	
	0,04493	0,05194	15,60	
	Average		**16,99**	*1,68*
Safflower	0,04727	0,05428	14,83	
	0,03352	0,03963	18,23	
	0,0452	0,05172	14,42	
	Average		**15,83**	*2,09*
Cochineal	0,05665	0,06418	13,29	
	0,04823	0,05456	13,12	
	0,0411	0,04635	12,77	
	Average		**13,06**	*0,26*
Comb.1	0,04003	0,04401	9,94	
	0,04456	0,05066	13,69	
	0,04452	0,04881	9,64	
	Average		**11,09**	*2,26*
Comb.2	0,04785	0,05543	15,84	
	0,04828	0,05331	10,42	
	0,04519	0,05122	13,34	
	Average		**13,20**	*2,71*
Comb.3	0,03063	0,03499	14,23	
	0,04602	0,0531	15,38	
	0,0427	0,04989	16,84	
	Average		**15,49**	*1,30*

B.2 Colour changes after treatment

B.2.1 Colourimetric measurements of samples treated with inhibitors through an Acetone solution

		before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	Standard deviation
Inhibitor A	L*1	108,45	108,72	0,27	a*1	-5,55	-6,38	-0,83	b*1	5,09	6,73	1,64	**1,86**	*0,30*
	L*2	108,59	108,4	-0,19	a*2	-5,65	-6,26	-0,61	b*2	4,87	7,23	2,36	**2,44**	
	L*3	108,48	108,66	0,18	a*3	-5,49	-6,38	-0,89	b*3	4,79	6,88	2,09	**2,28**	
	AvL*	108,51	108,59	0,09	Ava*	-5,56	-6,34	-0,78	Avb*	4,92	6,95	2,03	**2,18**	
Inhibitor B	L*1	108,52	108,55	0,03	a*1	-5,57	-6,46	-0,89	b*1	5,18	6,86	1,68	**1,90**	*0,38*
	L*2	108,5	108,27	-0,23	a*2	-5,51	-6,16	-0,65	b*2	5,06	7,54	2,48	**2,57**	
	L*3	108,47	108,42	-0,05	a*3	-5,52	-6,32	-0,8	b*3	5,08	6,82	1,74	**1,92**	
	AvL*	108,50	108,41	-0,08	Ava*	-5,53	-6,31	-0,78	Avb*	5,11	7,07	1,97	**2,12**	
Inhibitor D	L*1	108,56	108,5	-0,06	a*1	-5,65	-5,85	-0,2	b*1	5,03	6,37	1,34	**1,36**	*0,19*
	L*2	108,9	108,57	-0,33	a*2	-5,85	-5,95	-0,1	b*2	5,6	6,54	0,94	**1,00**	
	L*3	108,69	108,26	-0,43	a*3	-5,77	-5,74	0,03	b*3	5,19	6,39	1,2	**1,28**	
	AvL*	108,72	108,44	-0,27	Ava*	-5,76	-5,85	-0,09	Avb*	5,27	6,43	1,16	**1,20**	
Inhibitor E	L*1	108,69	108,05	-0,64	a*1	-5,71	-5,84	-0,13	b*1	5,08	6,79	1,71	**1,83**	*0,25*
	L*2	108,69	107,96	-0,73	a*2	-5,71	-5,74	-0,03	b*2	5,65	6,81	1,16	**1,37**	
	L*3	108,91	108,35	-0,56	a*3	-5,87	-6,06	-0,19	b*3	5,67	6,99	1,32	**1,45**	
	AvL*	108,76	108,12	-0,64	Ava*	-5,76	-5,88	-0,12	Avb*	5,47	6,86	1,40	**1,54**	
Inhibitor F	L*1	108,86	108,07	-0,79	a*1	-5,77	-6,39	-0,62	b*1	5,52	7,99	2,47	**2,67**	*0,19*
	L*2	108,85	108,08	-0,77	a*2	-5,8	-6,13	-0,33	b*2	5,62	8,21	2,59	**2,72**	
	L*3	108,83	108,24	-0,59	a*3	-5,81	-6,56	-0,75	b*3	5,7	8,57	2,87	**3,02**	
	AvL*	108,85	108,13	-0,72	Ava*	-5,79	-6,36	-0,57	Avb*	5,61	8,26	2,64	**2,80**	
Inhibitor G	L*1	108,57	107,96	-0,61	a*1	-5,67	-6,11	-0,44	b*1	5,7	8,12	2,42	**2,53**	*0,50*
	L*2	108,7	108,05	-0,65	a*2	-5,73	-6,04	-0,31	b*2	5,7	7,58	1,88	**2,01**	
	L*3	108,58	108,15	-0,43	a*3	-5,69	-6,09	-0,4	b*3	5,7	7,12	1,42	**1,54**	
	AvL*	108,62	108,05	-0,56	Ava*	-5,70	-6,08	-0,38	Avb*	5,70	7,61	1,91	**2,02**	

B.2.2 Colourimetric measurements of samples treated with inhibitors through an Ethanol solution

		before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	Standard deviation
Inhibitor A	L*1	116,05	115,94	-0,11	a*1	-10,41	-11,03	-0,62	b*1	6,13	7,67	1,54	**1,66**	*0,33*
	L*2	116,46	115,85	-0,61	a*2	-10,58	-10,94	-0,36	b*2	6,73	7,45	0,72	**1,01**	
	L*3	116,09	116,55	0,46	a*3	-10,46	-11,21	-0,75	b*3	6,26	7,41	1,15	**1,45**	
	AvL*	116,2	116,1133	-0,09	Ava*	-10,48	-11,06	-0,58	Avb*	6,37	7,51	1,14	**1,28**	
Inhibitor B	L*1	116,05	115,77	-0,28	a*1	-13,42	-10,75	2,67	b*1	8,78	7,7	-1,08	**2,89**	*1,46*
	L*2	119,4	115,82	-3,58	a*2	-10,4	-10,83	-0,43	b*2	6,26	7,02	0,76	**3,68**	
	L*3	116,05	115,95	-0,1	a*3	-10,4	-10,82	-0,42	b*3	6,26	6,99	0,73	**0,85**	
	AvL*	117,17	115,85	-1,32	Ava*	-11,41	-10,80	0,61	Avb*	7,10	7,24	0,14	**1,46**	
Inhibitor D	L*1	116,05	115,94	-0,11	a*1	-10,36	-10,89	-0,53	b*1	6,3	7,39	1,09	**1,22**	*0,19*
	L*2	116,3	115,87	-0,43	a*2	-10,63	-10,76	-0,13	b*2	6,97	7,71	0,74	**0,87**	
	L*3	116,4	115,47	-0,93	a*3	-10,4	-10,6	-0,2	b*3	6,43	7,07	0,64	**1,15**	
	AvL*	116,25	115,76	-0,49	Ava*	-10,46	-10,75	-0,29	Avb*	6,57	7,39	0,82	**1,00**	
Inhibitor G	L*1	108,18	108,41	0,23	a*1	-5,24	-5,84	-0,6	b*1	5,08	6,73	1,65	**1,77**	*0,39*
	L*2	109,02	108,36	-0,66	a*2	-5,72	-5,85	-0,13	b*2	5,41	6,53	1,12	**1,31**	
	L*3	109,02	107,87	-1,15	a*3	-5,72	-5,71	0,01	b*3	5,39	7,13	1,74	**2,09**	
	AvL*	108,74	108,21	-0,53	Ava*	-5,56	-5,80	-0,24	Avb*	5,29	6,80	1,50	**1,61**	

B.2.3 Colourimetric measurements of samples treated with inhibitors through a Tetrachloroethylene solution

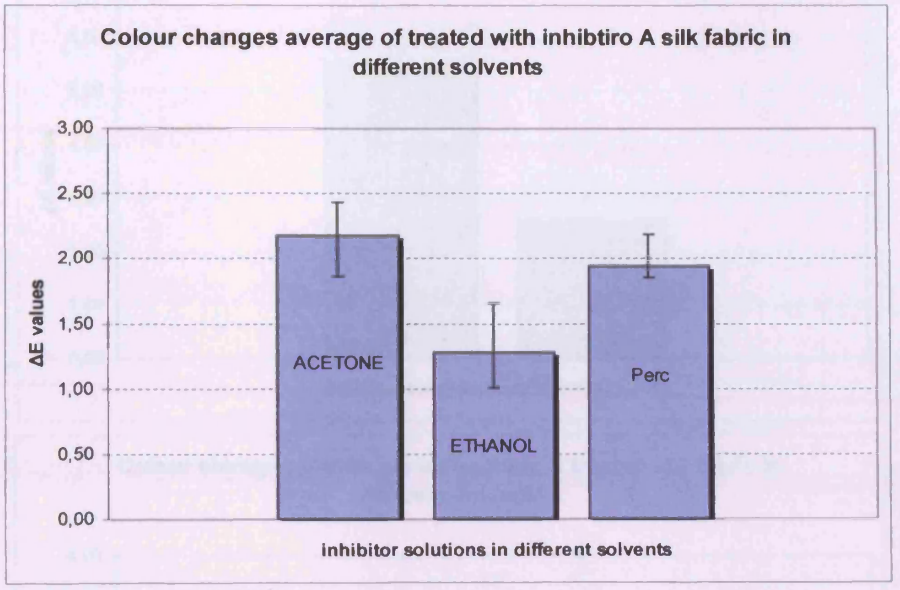
		before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	Standard deviation
Inhibitor A	L*1	108,27	108,74	0,47	a*1	-5,51	-6,47	-0,96	b*1	5,33	6,84	1,51	**1,85**	*0,19*
	L*2	108,83	108,02	-0,81	a*2	-5,8	-5,97	-0,17	b*2	5,42	7,45	2,03	**2,19**	
	L*3	108,76	107,93	-0,83	a*3	-5,84	-5,95	-0,11	b*3	5,43	7,44	2,01	**2,18**	
	AvL*	108,62	108,23	-0,39	Ava*	-5,72	-6,13	-0,41	Avb*	5,39	7,24	1,85	**1,94**	
Inhibitor B	L*1	109,04	108,3	-0,74	a*1	-5,93	-6,24	-0,31	b*1	5,35	7,07	1,72	**1,90**	*0,42*
	L*2	108,57	108,54	-0,03	a*2	-5,61	-6,34	-0,73	b*2	5,37	7,93	2,56	**2,66**	
	L*3	108,73	108,61	-0,12	a*3	-5,64	-6,33	-0,69	b*3	5,57	7,41	1,84	**1,97**	
	AvL*	108,78	108,48	-0,30	Ava*	-5,73	-6,30	-0,58	Avb*	5,43	7,47	2,04	**2,14**	
Inhibitor C	L*1	108,64	108,36	-0,28	a*1	-5,66	-7,48	-1,82	b*1	5,35	10,5	5,15	**5,47**	*0,32*
	L*2	108,46	108,23	-0,23	a*2	-5,58	-7,7	-2,12	b*2	5,51	11,01	5,5	**5,90**	
	L*3	108,57	108,84	0,27	a*3	-5,66	-7,84	-2,18	b*3	5,59	10,38	4,79	**5,27**	
	AvL*	108,56	108,48	-0,08	Ava*	-5,63	-7,67	-2,04	Avb*	5,48	10,63	5,15	**5,54**	
Inhibitor D	L*1	108,82	108,59	-0,23	a*1	-5,79	-6,02	-0,23	b*1	5,61	7,2	1,59	**1,62**	*1,33*
	L*2	108,64	108,32	-0,32	a*2	-5,69	-6,89	-1,2	b*2	5,58	8,79	3,21	**3,44**	
	L*3	108,71	108,23	-0,48	a*3	-5,77	-5,72	0,05	b*3	5,59	6,29	0,7	**0,85**	
	AvL*	108,72	108,38	-0,34	Ava*	-5,75	-6,21	-0,46	Avb*	5,59	7,43	1,83	**1,92**	
Inhibitor E	L*1	100,03	99,69	-0,34	a*1	-1,04	-1,59	-0,55	b*1	1,91	4,21	2,3	**2,39**	*0,48*
	L*2	99,9	100,07	0,17	a*2	-0,98	-1,44	-0,46	b*2	2,06	3,44	1,38	**1,46**	
	L*3	100,09	100,03	-0,06	a*3	-1,03	-1,4	-0,37	b*3	2,17	3,82	1,65	**1,69**	
	AvL*	100,01	99,93	-0,08	Ava*	-1,02	-1,48	-0,46	Avb*	2,05	3,82	1,78	**1,84**	

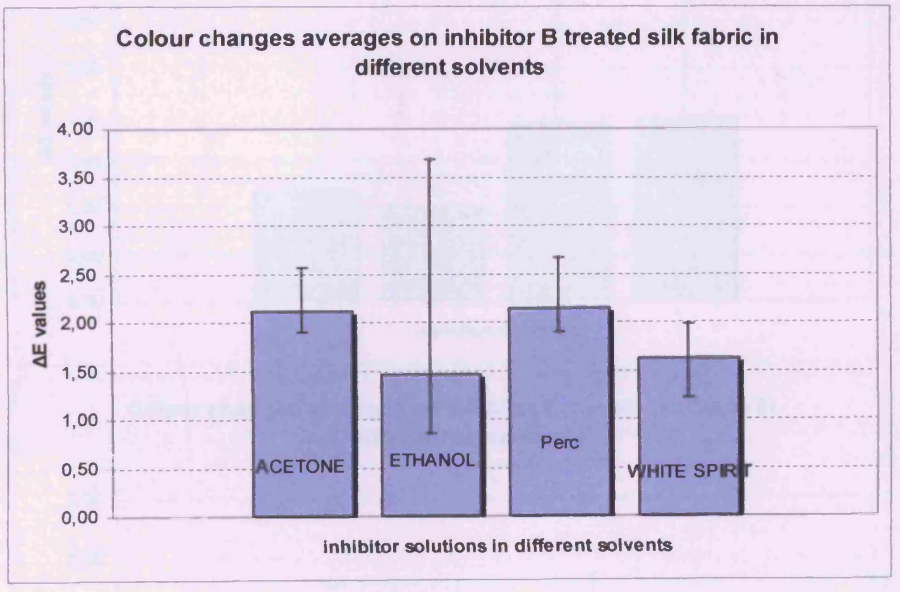
		before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	Standard deviation
Inhibitor F	L*1	100,05	100,03	-0,02	a*1	-1,09	-1,7	-0,61	b*1	2,59	4,12	1,53	**1,65**	*0,06*
	L*2	99,98	99,92	-0,06	a*2	-1,06	-1,69	-0,63	b*2	2,44	4,1	1,66	**1,78**	
	L*3	99,94	99,8	-0,14	a*3	-1,1	-1,64	-0,54	b*3	2,56	4,17	1,61	**1,70**	
	AvL*	99,99	99,92	-0,07	Ava*	-1,08	-1,68	-0,59	Avb*	2,53	4,13	1,60	**1,71**	
Inhibitor G	L*1	100,36	100,43	0,07	a*1	-1,24	-1,9	-0,66	b*1	2,42	4,07	1,65	**1,78**	*0,41*
	L*2	99,64	99,92	0,28	A*2	-0,94	-1,84	-0,9	b*2	2,25	4,43	2,18	**2,38**	
	L*3	100,01	100,22	0,21	A*3	-1,08	-1,78	-0,7	b*3	2,42	3,84	1,42	**1,60**	
	AvL*	100,00	100,19	0,19	Ava*	-1,09	-1,84	-0,75	Avb*	2,36	4,11	1,75	**1,91**	
Inhibitor H	L*1	100,16	99,53	-0,63	a*1	-1,09	-2,84	-1,75	b*1	2,31	8,12	5,81	**6,10**	*0,91*
	L*2	100,19	99,73	-0,46	a*2	-1,15	-2,75	-1,6	b*2	2,28	7,01	4,73	**5,01**	
	L*3	100,09	99,76	-0,33	a*3	-1,08	-2,38	-1,3	b*3	2,39	6,46	4,07	**4,29**	
	AvL*	100,15	99,67	-0,47	Ava*	-1,11	-2,66	-1,55	Avb*	2,33	7,20	4,87	**5,13**	
Inhibitor I	L*1	100,13	100,03	-0,1	a*1	-1,03	-2,66	-1,63	b*1	2,18	6,37	4,19	**4,50**	*0,11*
	L*2	100,2	99,72	-0,48	a*2	-1,14	-2,09	-0,95	b*2	2,2	6,36	4,16	**4,29**	
	L*3	100,39	99,68	-0,71	a*3	-1,19	-2,13	-0,94	b*3	2,12	6,41	4,29	**4,45**	
	AvL*	100,24	99,81	-0,43	Ava*	-1,12	-2,29	-1,17	Avb*	2,17	6,38	4,21	**4,39**	

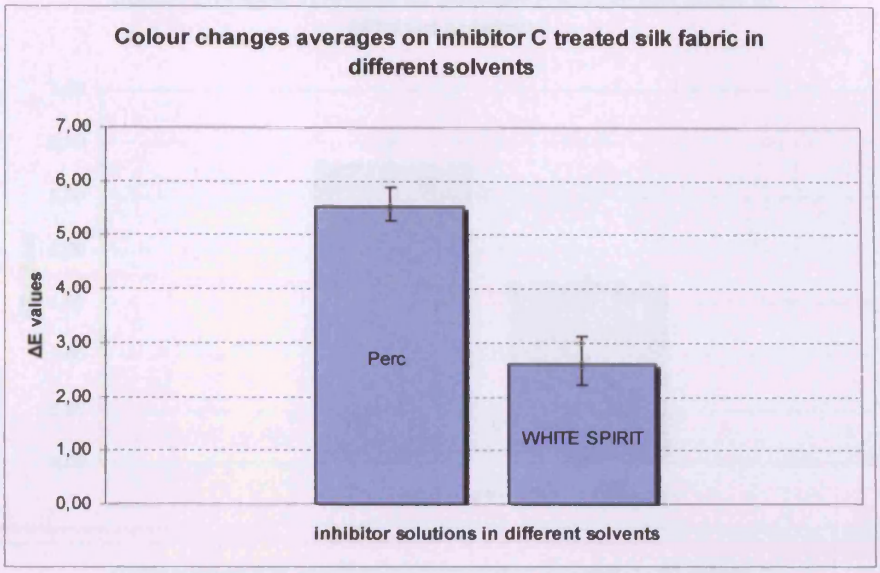
B.2.4 Colourimetric measurements of samples treated with inhibitors through a White Spirit solution

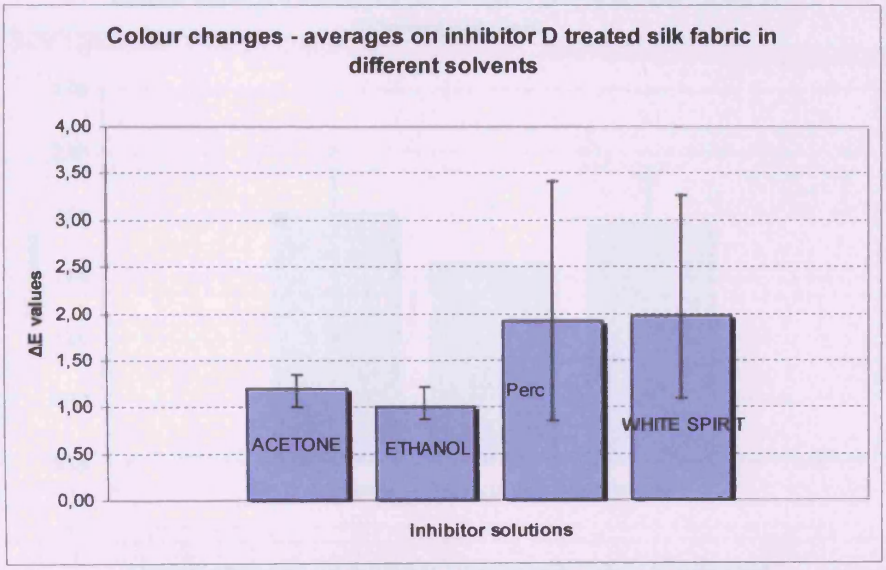
		before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	Standard deviation
Inhibitor B	L*1	100,22	99,76	-0,46	a*1	-1,15	-1,46	-0,31	b*1	1,89	3,8	1,91	**1,99**	*0,39*
	L*2	100,02	100,11	0,09	a*2	-1,09	-1,48	-0,39	b*2	1,85	3	1,15	**1,22**	
	L*3	99,94	99,76	-0,18	a*3	-1,15	-1,45	-0,3	b*3	2	3,66	1,66	**1,70**	
	AvL*	100,06	99,88	-0,18	Ava*	-1,13	-1,46	-0,33	Avb*	1,91	3,49	1,57	**1,62**	
Inhibitor C	L*1	100,47	100,04	-0,43	a*1	-1,33	-1,68	-0,35	b*1	2,11	4,25	2,14	**2,21**	*0,47*
	L*2	100,21	99,82	-0,39	a*2	-1,29	-1,91	-0,62	b*2	2,12	4,52	2,4	**2,51**	
	L*3	100,11	99,97	-0,14	a*3	-1,2	-2,09	-0,89	b*3	1,97	4,97	3	**3,13**	
	AvL*	100,26	99,94	-0,32	Ava*	-1,27	-1,89	-0,62	Avb*	2,07	4,58	2,51	**2,61**	
Inhibitor D	L*1	100,38	100,23	-0,15	a*1	-1,32	-1,34	-0,02	b*1	2,26	3,35	1,09	**1,10**	*1,13*
	L*2	100,39	100,12	-0,27	a*2	-1,32	-1,37	-0,05	b*2	2,31	3,87	1,56	**1,58**	
	L*3	100,18	99,52	-0,66	a*3	-1,23	-1,54	-0,31	b*3	2,14	5,32	3,18	**3,26**	
	AvL*	100,32	99,96	-0,36	Ava*	-1,29	-1,42	-0,13	Avb*	2,24	4,18	1,94	**1,98**	
Inhibitor I	L*1	100,3	100,09	-0,21	a*1	-1,26	-2,43	-1,17	b*1	2,27	6,16	3,89	**4,07**	*0,20*
	L*2	100,14	99,78	-0,36	a*2	-1,2	-2,37	-1,17	b*2	2,09	6,25	4,16	**4,34**	
	L*3	100,26	99,7	-0,56	a*3	-1,37	-2,6	-1,23	b*3	2,36	6,62	4,26	**4,47**	
	AvL*	100,23	99,86	-0,38	Ava*	-1,28	-2,47	-1,19	Avb*	2,24	6,34	4,10	**4,29**	

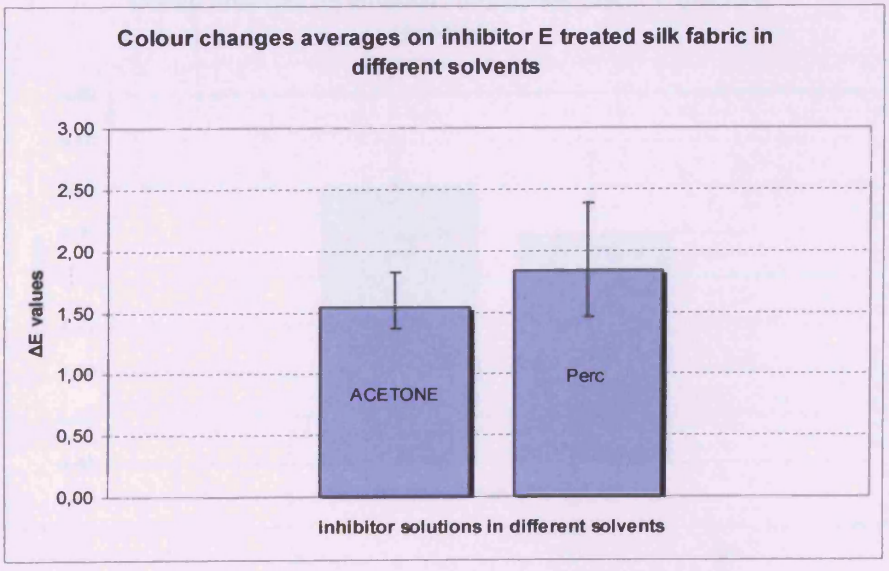
B.2.5 Graphs showing colour changes averages on treated with inhibitor silk fabric through different solvent solutions

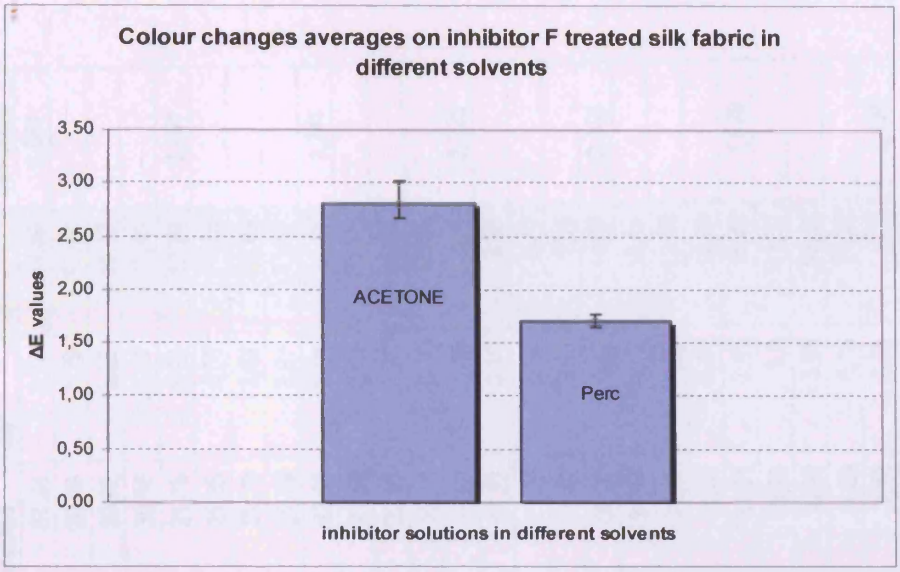


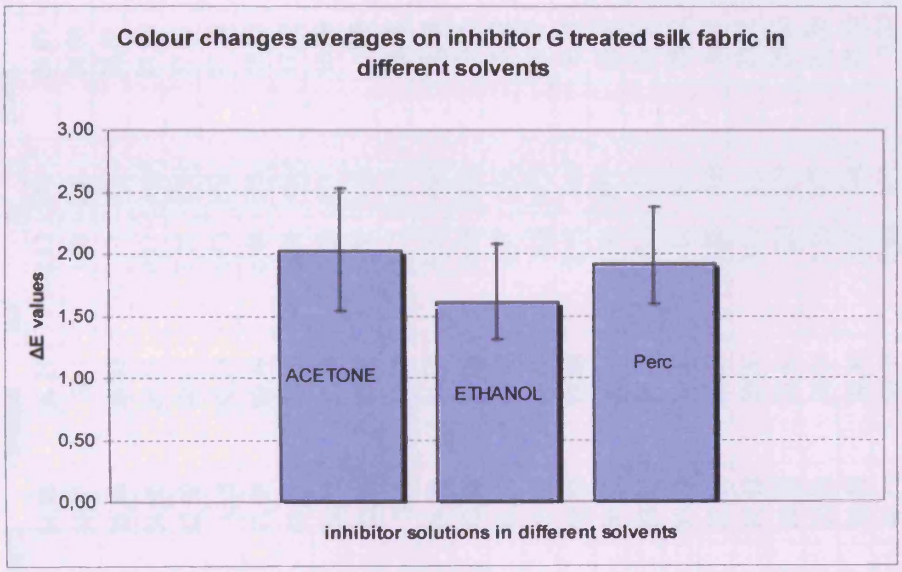


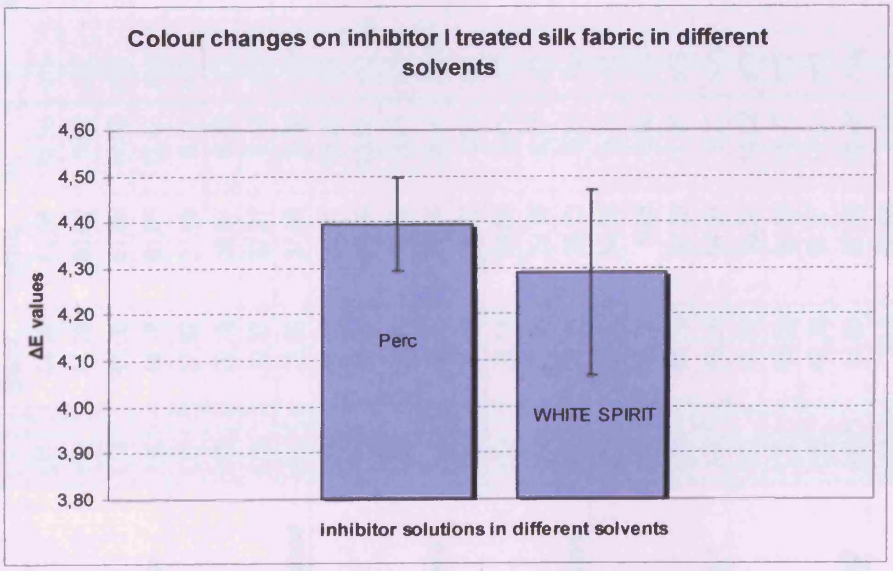

Colour changes averages on inhibitor C treated silk fabric in different solvents
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
Perc
WHITE SPIRIT
inhibitor solutions in different solvents


Colour changes - averages on inhibitor D treated silk fabric in different solvents
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
ΔE values
ACETONE
ETHANOL
Perc
WHITE SPIRIT
inhibitor solutions


Colour changes averages on inhibitor E treated silk fabric in different solvents
3,00
2,50
2,00
1,50
1,00
0,50
0,00
ΔE values
ACETONE
Perc
inhibitor solutions in different solvents


Colour changes averages on inhibitor F treated silk fabric in different solvents
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
ΔE values
ACETONE
Perc
inhibitor solutions in different solvents


Colour changes averages on inhibitor G treated silk fabric in different solvents
3,00
2,50
2,00
1,50
1,00
0,50
0,00
ΔE values
ACETONE
ETHANOL
Perc
inhibitor solutions in different solvents


Colour changes on inhibitor I treated silk fabric in different solvents
4,60
4,50
4,40
4,30
4,20
4,10
4,00
3,90
3,80
ΔE values
Perc
WHITE SPIRIT
inhibitor solutions in different solvents

B.2.6 Colourimetric measurements of samples treated with inhibitor A

		Blank	treated	ΔL		Blank	treated	Δa*		Blank	treated	Δb*	ΔE	Standard deviation
	L*1	44,18	62,56	18,38	a*1	34,34	34,21	-0,13	b*1	24,61	31,38	6,77	19,59	*1,061*
	L*2	44,29	60,69	16,4	a*2	33,07	34,7	1,63	b*2	24,69	30,48	5,79	17,47	
	L*3	44,06	61,69	17,63	a*3	35,33	34,33	-1	b*3	25,67	30,92	5,25	18,42	
Madder	AvL*	44,18	61,65	17,47	Ava*	34,25	34,41	0,17	Avb*	24,99	30,93	5,94	18,49	
	L*1	27,92	37,69	9,77	a*1	42,19	49,45	7,26	b*1	17,83	21,75	3,92	12,79	*1,091*
	L*2	29,28	38,07	8,79	a*2	43,5	49,23	5,73	b*2	17,79	21,85	4,06	11,25	
	L*3	29,37	37,81	8,44	a*3	43,95	49,39	5,44	b*3	18,15	21,78	3,63	10,68	
Brazilwood	AvL*	28,86	37,86	9,00	Ava*	43,21	49,36	6,14	Avb*	17,92	21,79	3,87	11,57	
	L*1	63,75	80,01	16,26	a*1	24,92	30,15	5,23	b*1	15,99	22,45	6,46	18,26	*1,241*
	L*2	66,93	79,99	13,06	a*2	23,85	30,67	6,82	b*2	15,8	21,48	5,68	15,79	
	L*3	66,01	79,22	13,21	a*3	24,4	32,31	7,91	b*3	15,85	22,61	6,76	16,82	
Safflower	AvL*	65,56	79,74	14,18	Ava*	24,39	31,04	6,65	Avb*	15,88	22,18	6,30	16,96	
	L*1	24,85	30,76	5,91	a*1	43,56	44,04	0,48	b*1	10,85	10,83	-0,02	5,93	*2,225*
	L*2	26,14	29,86	3,72	a*2	44,26	44,93	0,67	b*2	10,32	11,23	0,91	3,89	
	L*3	23,68	29,76	6,08	a*3	40,22	45,62	5,4	b*3	9,47	11,29	1,82	8,33	
Cochineal	AvL*	24,89	30,13	5,24	Ava*	42,68	44,86	2,18	Avb*	10,21	11,12	0,90	6,05	
	L*1	44,99	54,53	9,54	a*1	30,87	39,31	8,44	b*1	25,16	30,97	5,81	14,00	*2,055*
	L*2	46,78	53,6	6,82	a*2	33,41	39,71	6,3	b*2	26,97	31,14	4,17	10,18	
	L*3	44,29	55,58	11,29	a*3	33,22	39,05	5,83	b*3	26,92	31,17	4,25	13,40	
Comb. 1	AvL*	45,35	54,57	9,22	Ava*	32,50	39,36	6,86	Avb*	26,35	31,09	4,74	12,53	
	L*1	42,53	56,55	14,02	a*1	28,43	32,36	3,93	b*1	23,76	31,41	7,65	16,45	*1,879*
	L*2	45,09	56,86	11,77	a*2	29,23	32,53	3,3	b*2	25,03	30,93	5,9	13,57	
	L*3	46,36	57,87	11,51	a*3	30,61	32,54	1,93	b*3	25,39	30,92	5,53	12,91	
Comb.2	AvL*	44,66	57,09	12,43	Ava*	29,42	32,48	3,05	Avb*	24,73	31,09	6,36	14,31	
	L*1	30,2	33,68	3,48	a*1	46,71	52,35	5,64	b*1	3,33	7,18	3,85	7,66	*2,438*
	L*2	30,44	34,08	3,64	a*2	48,76	52,74	3,98	b*2	4,97	6,82	1,85	5,70	
	L*3	27,05	33,1	6,05	a*3	44,44	52,22	7,78	b*3	3,87	7,63	3,76	10,55	
Comb. 3	AvL*	29,23	33,62	4,39	Ava*	46,64	52,44	5,80	Avb*	4,06	7,21	3,15	7,97	

B.2.7 Colourimetric measurements of samples treated with inhibitor B

		Blank	treated	ΔL*		Blank	treated	Δa*		Blank	treated	Δb*	ΔE	Standard deviation
	L*1	44,18	64,76	20,58	a*1	34,34	32,32	-2,02	b*1	24,61	30,69	6,08	**21,55**	*1,24*
	L*2	44,29	65,56	21,27	a*2	33,07	30,05	-3,02	b*2	24,69	29,17	4,48	**21,95**	
	L*3	44,06	62,88	18,82	a*3	35,33	34,55	-0,78	b*3	25,67	31,17	5,5	**19,62**	
Madder	AvL*	44,18	64,40	20,22	Ava*	34,25	32,31	-1,94	Avb*	24,99	30,34	5,35	**21,04**	
	L*1	27,92	36,31	8,39	a*1	42,19	46,29	4,1	b*1	17,83	19,48	1,65	**9,48**	*0,94*
	L*2	29,28	36,79	7,51	a*2	43,5	46,62	3,12	b*2	17,79	19,62	1,83	**8,34**	
	L*3	29,37	36,3	6,93	a*3	43,95	46,6	2,65	b*3	18,15	19,84	1,69	**7,61**	
Brazilwood	AvL*	28,86	36,47	7,61	Ava*	43,21	46,50	3,29	Avb*	17,92	19,65	1,72	**8,48**	
	L*1	63,75	79,93	16,18	a*1	24,92	30,77	5,85	b*1	15,99	20,76	4,77	**17,85**	*1,13*
	L*2	66,93	79,95	13,02	a*2	23,85	31,11	7,26	b*2	15,8	20,75	4,95	**15,71**	
	L*3	66,01	80,11	14,1	a*3	24,4	30,61	6,21	b*3	15,85	20,8	4,95	**16,18**	
Safflower	AvL*	65,56	80,00	14,43	Ava*	24,39	30,83	6,44	Avb*	15,88	20,77	4,89	**16,58**	
	L*1	24,85	31,16	6,31	a*1	43,56	44,5	0,94	b*1	10,85	9,7	-1,15	**6,48**	*1,20*
	L*2	26,14	30,81	4,67	a*2	44,26	43,95	-0,31	b*2	10,32	9,49	-0,83	**4,75**	
	L*3	23,68	29,8	6,12	a*3	40,22	43,72	3,5	b*3	9,47	9,71	0,24	**7,05**	
Cochineal	AvL*	24,89	30,59	5,7	Ava*	42,68	44,06	1,38	Avb*	10,21	9,63	-0,58	**6,10**	
	L*1	44,99	55,83	10,84	a*1	30,87	36,29	5,42	b*1	25,16	31,24	6,08	**13,56**	*2,02*
	L*2	46,78	55,42	8,64	a*2	33,41	36,36	2,95	b*2	26,97	30,32	3,35	**9,72**	
	L*3	44,29	56,61	12,32	a*3	33,22	34,74	1,52	b*3	26,92	29,78	2,86	**12,74**	
Comb. 1	AvL*	45,35	55,95	10,6	Ava*	32,50	35,80	3,30	Avb*	26,35	30,45	4,10	**12,01**	
	L*1	42,53	56,71	14,18	a*1	28,43	32,65	4,22	b*1	23,76	30,95	7,19	**16,45**	*3,34*
	L*2	45,09	24,67	20,42	a*2	29,23	31,79	2,56	b*2	25,03	30,39	5,36	**21,27**	
	L*3	46,36	24,37	21,99	a*3	30,61	32,96	2,35	b*3	25,39	31,2	5,81	**22,87**	
Comb.2	AvL*	44,66	35,25	-9,41	Ava*	29,42	32,47	3,04	Avb*	24,73	30,85	6,12	**20,19**	
	L*1	30,2	32,98	2,78	a*1	46,71	51,37	4,66	b*1	3,33	6,48	3,15	**6,27**	*2,78*
	L*2	30,44	32,3	1,86	a*2	48,76	49,93	1,17	b*2	4,97	6,91	1,94	**2,93**	
	L*3	27,05	32,73	5,68	a*3	44,44	50,11	5,67	b*3	3,87	6,51	2,64	**8,45**	
Comb. 3	AvL*	29,23	32,67	3,44	Ava*	46,64	50,47	3,83	Avb*	4,06	6,63	2,58	**5,88**	

B.2.8 Colourimetric measurements of samples treated with inhibitor C

		Blank	treated	ΔL*		Blank	treated	Δa*		Blank	treated	Δb*	ΔE	Standard deviation
	L*1	44,18	55,01	10,83	a*1	34,34	40,72	6,38	b*1	24,61	28,95	4,34	13,30	*1,02*
	L*2	44,29	56,22	11,93	a*2	33,07	40,18	7,11	b*2	24,69	28,92	4,23	14,52	
	L*3	44,06	55,27	11,21	a*3	35,33	40,21	4,88	b*3	25,67	28,21	2,54	12,49	
Madder	AvL*	44,18	55,50	11,32	Ava*	34,25	40,37	6,12	Avb*	24,99	28,69	3,70	13,43	
	L*1	27,92	37,05	9,13	a*1	42,19	44,8	2,61	b*1	17,83	18,22	0,39	9,50	*0,83*
	L*2	29,28	37,7	8,42	a*2	43,5	44,71	1,21	b*2	17,79	18,17	0,38	8,51	
	L*3	29,37	37,21	7,84	a*3	43,95	44,44	0,49	b*3	18,15	17,86	-0,29	7,86	
Brazilwood	AvL*	28,86	37,32	8,46	Ava*	43,21	44,65	1,44	Avb*	17,92	18,08	0,16	8,63	
	L*1	63,75	79,39	15,64	a*1	24,92	31,55	6,63	b*1	15,99	21,29	5,3	17,79	*1,02*
	L*2	66,93	80,61	13,68	a*2	23,85	30,28	6,43	b*2	15,8	20,57	4,77	15,85	
	L*3	66,01	79,9	13,89	a*3	24,4	31,38	6,98	b*3	15,85	20,77	4,92	16,31	
Safflower	AvL*	65,56	79,97	14,40	Ava*	24,39	31,07	6,68	Avb*	15,88	20,88	5,00	16,65	
	L*1	24,85	33,09	8,24	a*1	43,56	41,49	-2,07	b*1	10,85	8,31	-2,54	8,87	*0,07*
	L*2	26,14	33,14	7	a*2	44,26	39,76	-4,5	b*2	10,32	7,06	-3,26	8,94	
	L*3	23,68	32,42	8,74	a*3	40,22	40,17	-0,05	b*3	9,47	7,27	-2,2	9,01	
Cochineal	AvL*	24,89	32,88	7,99	Ava*	42,68	40,47	-2,21	Avb*	10,21	7,55	-2,67	8,94	
	L*1	44,99	56,79	11,8	a*1	30,87	37,07	6,2	b*1	25,16	29,59	4,43	14,05	*1,58*
	L*2	46,78	56,86	10,08	a*2	33,41	37,06	3,65	b*2	26,97	29,36	2,39	10,98	
	L*3	44,29	57,19	12,9	a*3	33,22	35,67	2,45	b*3	26,92	28,31	1,39	13,20	
Comb. 1	AvL*	45,35	56,95	11,59	Ava*	32,5	36,60	4,10	Avb*	26,35	29,09	2,74	12,74	
	L*1	42,53	56,38	13,85	a*1	28,43	32,33	3,9	b*1	23,76	27,19	3,43	14,79	*3,01*
	L*2	45,09	53,36	8,27	a*2	29,23	34,7	5,47	b*2	25,03	26,35	1,32	10,00	
	L*3	46,36	55,18	8,82	a*3	30,61	33,29	2,68	b*3	25,39	26,15	0,76	9,25	
Comb.2	AvL*	44,66	54,97	10,31	Ava*	29,42	33,44	4,02	Avb*	24,73	26,56	1,84	11,35	
	L*1	30,2	36,36	6,16	a*1	46,71	46,89	0,18	b*1	3,33	3,3	-0,03	6,16	*2,29*
	L*2	30,44	35,61	5,17	a*2	48,76	46,62	-2,14	b*2	4,97	5,3	0,33	5,61	
	L*3	27,05	36,62	9,57	a*3	44,44	46,59	2,15	b*3	3,87	3,36	-0,51	9,82	
Comb. 3	AvL*	29,23	36,20	6,97	Ava*	46,64	46,70	0,06	Avb*	4,06	3,99	-0,07	7,20	

B.2.9 Colourimetic measurements of samples treated with inhibitor D

		Blank	treated	ΔL*		Blank	treated	Δa*		Blank	treated	Δb*	ΔE	Standard deviation
	L*1	44,18	55,36	11,18	a*1	34,34	40,41	6,07	b*1	24,61	32,29	7,68	**14,86**	*0,33*
	L*2	44,29	55,44	11,15	a*2	33,07	40,45	7,38	b*2	24,69	32,06	7,37	**15,27**	
	L*3	44,06	56,65	12,59	a*3	35,33	39,34	4,01	b*3	25,67	31,9	6,23	**14,61**	
Madder	AvL*	44,18	55,82	11,64	Ava*	34,25	40,07	5,82	Avb*	24,99	32,08	7,09	**14,91**	
	L*1	27,92	35,45	7,53	a*1	42,19	48,08	5,89	b*1	17,83	18,93	1,1	**9,62**	*1,51*
	L*2	29,28	34,42	5,14	a*2	43,5	47,84	4,34	b*2	17,79	18,6	0,81	**6,78**	
	L*3	29,37	35,83	6,46	a*3	43,95	47,45	3,5	b*3	18,15	18,38	0,23	**7,35**	
Brazilwood	AvL*	28,86	35,23	6,38	Ava*	43,21	47,79	4,58	Avb*	17,92	18,64	0,71	**7,92**	
	L*1	63,75	79,81	16,06	a*1	24,92	31,26	6,34	b*1	15,99	21,23	5,24	**18,04**	*1,16*
	L*2	66,93	79,65	12,72	a*2	23,85	31,82	7,97	b*2	15,8	20,52	4,72	**15,74**	
	L*3	66,01	80,9	14,89	a*3	24,4	30,54	6,14	b*3	15,85	20,45	4,6	**16,75**	
Safflower	AvL*	65,56	80,12	14,56	Ava*	24,39	31,21	6,82	Avb*	15,88	20,73	4,85	**16,84**	
	L*1	24,85	30,16	5,31	a*1	43,56	45,48	1,92	b*1	10,85	12,08	1,23	**5,78**	*1,72*
	L*2	26,14	29,16	3,02	a*2	44,26	42,95	-1,31	b*2	10,32	11,2	0,88	**3,41**	
	L*3	23,68	29,83	6,15	a*3	40,22	42,6	2,38	b*3	9,47	10,94	1,47	**6,76**	
Cochineal	AvL*	24,89	29,72	4,83	Ava*	42,68	43,68	1,00	Avb*	10,21	11,41	1,19	**5,31**	
	L*1	44,99	56,79	11,8	a*1	30,87	37,07	6,2	b*1	25,16	29,59	4,43	**14,05**	*1,58*
	L*2	46,78	56,86	10,08	a*2	33,41	37,06	3,65	b*2	26,97	29,36	2,39	**10,98**	
	L*3	44,29	57,19	12,9	a*3	33,22	35,67	2,45	b*3	26,92	28,31	1,39	**13,20**	
Comb. 1	AvL*	45,35	56,95	11,59	Ava*	32,50	36,60	4,10	Avb*	26,35	29,09	2,74	**12,74**	
	L*1	42,53	53,14	10,61	a*1	28,43	35,37	6,94	b*1	23,76	31,46	7,7	**14,83**	*2,31*
	L*2	45,09	52,88	7,79	a*2	29,23	35,79	6,56	b*2	25,03	30,8	5,77	**11,71**	
	L*3	46,36	53,17	6,81	a*3	30,61	35,51	4,9	b*3	25,39	31,42	6,03	**10,33**	
Comb.2	AvL*	44,66	53,06	8,40	Ava*	29,42	35,56	6,13	Avb*	24,73	31,23	6,50	**12,29**	
	L*1	30,2	29,63	-0,57	a*1	46,71	49,13	2,42	b*1	3,33	10,29	6,96	**7,39**	*1,62*
	L*2	30,44	30,89	0,45	a*2	48,76	49,83	1,07	b*2	4,97	10,01	5,04	**5,17**	
	L*3	27,05	30,61	3,56	a*3	44,44	48,66	4,22	b*3	3,87	10,09	6,22	**8,32**	
Comb. 3	AvL*	29,23	30,38	1,15	Ava*	46,64	49,21	2,57	Avb*	4,06	10,13	6,07	**6,96**	

B.2.10 Colourimetric measurements of samples treated with inhibitor E

		Blank	treated	ΔL*		Blank	treated	Δa*		Blank	treated	Δb*	ΔE	Standard deviation
	L*1	44,18	55,94	11,76	a*1	34,34	41,33	6,99	b*1	24,61	31,19	6,58	**15,18**	*1,20*
	L*2	44,29	55,47	11,18	a*2	33,07	41,1	8,03	b*2	24,69	30,98	6,29	**15,13**	
	L*3	44,06	54,94	10,88	a*3	35,33	40,76	5,43	b*3	25,67	30,51	4,84	**13,09**	
Madder	AvL*	44,18	55,45	11,27	Ava*	34,25	41,06	6,82	Avb*	24,99	30,89	5,90	**14,47**	
	L*1	27,92	34,52	6,6	a*1	42,19	45,5	3,31	b*1	17,83	18,26	0,43	**7,40**	0,96
	L*2	29,28	35,25	5,97	a*2	43,5	46,2	2,7	b*2	17,79	18,49	0,7	**6,59**	
	L*3	29,37	34,37	5	a*3	43,95	46,11	2,16	b*3	18,15	18,71	0,56	**5,48**	
Brazilwood	AvL*	28,86	34,71	5,86	Ava*	43,21	45,94	2,72	Avb*	17,92	18,49	0,56	**6,49**	
	L*1	63,75	79,67	15,92	a*1	24,92	31,09	6,17	b*1	15,99	20,32	4,33	**17,61**	1,19
	L*2	66,93	79,2	12,27	a*2	23,85	31,55	7,7	b*2	15,8	20,71	4,91	**15,30**	
	L*3	66,01	79,42	13,41	a*3	24,4	31,71	7,31	b*3	15,85	20,5	4,65	**15,97**	
Safflower	AvL*	65,56	79,43	13,87	Ava*	24,39	31,45	7,06	Avb*	15,88	20,51	4,63	**16,29**	
	L*1	24,85	28,95	4,1	a*1	43,56	41,95	-1,61	b*1	10,85	10,3	-0,55	**4,44**	0,97
	L*2	26,14	29,2	3,06	a*2	44,26	42,58	-1,68	b*2	10,32	10,4	0,08	**3,49**	
	L*3	23,68	28,53	4,85	a*3	40,22	42,5	2,28	b*3	9,47	10,37	0,9	**5,43**	
Cochineal	AvL*	24,89	28,89	4,00	Ava*	42,68	42,34	-0,34	Avb*	10,21	10,36	0,14	**4,45**	
	L*1	44,99	55,57	10,58	a*1	30,87	38,77	7,9	b*1	25,16	32,56	7,4	**15,14**	1,88
	L*2	46,78	56,39	9,61	a*2	33,41	37,6	4,19	b*2	26,97	32,19	5,22	**11,71**	
	L*3	44,29	57,19	12,9	a*3	33,22	38,22	5	b*3	26,92	32,14	5,22	**14,79**	
Comb. 1	AvL*	45,35	56,38	11,03	Ava*	32,50	38,20	5,70	Avb*	26,35	32,30	5,95	**13,88**	
	L*1	42,53	50,98	8,45	a*1	28,43	38,73	10,3	b*1	23,76	30,91	7,15	**15,12**	2,05
	L*2	45,09	52,1	7,01	a*2	29,23	38,17	8,94	b*2	25,03	31,88	6,85	**13,27**	
	L*3	46,36	51,9	5,54	a*3	30,61	38,02	7,41	b*3	25,39	31,39	6	**11,03**	
Comb.2	AvL*	44,66	51,66	7	Ava*	29,42	38,31	8,88	Avb*	24,73	31,39	6,67	**13,14**	
	L*1	30,2	30,75	0,55	a*1	46,71	47,33	0,62	b*1	3,33	9,37	6,04	**6,10**	1,47
	L*2	30,44	30,97	0,53	a*2	48,76	48,07	-0,69	b*2	4,97	8,37	3,4	**3,51**	
	L*3	27,05	30,82	3,77	a*3	44,44	47,4	2,96	b*3	3,87	7,48	3,61	**6,00**	
Comb. 3	AvL*	29,23	30,85	1,62	Ava*	46,64	47,60	0,96	Avb*	4,06	8,41	4,35	**5,20**	

B.2.11 Colourimetic measurements of samples treated with inhibitor F

		Blank	treated	ΔL		Blank	treated	Δa		Blank	treated	Δb	ΔE	Standard deviation
	L*1	44,18	56,93	12,75	a*1	34,34	38,82	4,48	b*1	24,61	30,73	6,12	**14,84**	*0,82*
	L*2	44,29	57,8	13,51	a*2	33,07	38,84	5,77	b*2	24,69	31,37	6,68	**16,14**	
	L*3	44,06	57,24	13,18	a*3	35,33	38,55	3,22	b*3	25,67	31,14	5,47	**14,63**	
Madder	AvL*	44,18	57,32	13,15	Ava*	34,25	38,74	4,49	Avb*	24,99	31,08	6,09	**15,20**	
	L*1	27,92	35,43	7,51	a*1	42,19	44,49	2,3	b*1	17,83	17,1	-0,73	**7,89**	*0,86*
	L*2	29,28	35,6	6,32	a*2	43,5	44,43	0,93	b*2	17,79	17,07	-0,72	**6,43**	
	L*3	29,37	35,62	6,25	a*3	43,95	44,26	0,31	b*3	18,15	16,91	-1,24	**6,38**	
Brazilwood	AvL*	28,86	35,55	6,69	Ava*	43,21	44,39	1,18	Avb*	17,92	17,03	-0,90	**6,90**	
	L*1	63,75	79,03	15,28	a*1	24,92	31,66	6,74	b*1	15,99	20,79	4,8	**17,38**	*1,13*
	L*2	66,93	78,91	11,98	a*2	23,85	31,76	7,91	b*2	15,8	20,6	4,8	**15,14**	
	L*3	66,01	78,94	12,93	a*3	24,4	32,28	7,88	b*3	15,85	21,15	5,3	**16,04**	
Safflower	AvL*	65,56	78,96	13,40	Ava*	24,39	31,90	7,51	Avb*	15,88	20,85	4,97	**16,19**	
	L*1	24,85	28,3	3,45	a*1	43,56	42,62	-0,94	b*1	10,85	10,38	-0,47	**3,61**	*1,45*
	L*2	26,14	27,85	1,71	a*2	44,26	42,63	-1,63	b*2	10,32	10,93	0,61	**2,44**	
	L*3	23,68	28,4	4,72	a*3	40,22	42,46	2,24	b*3	9,47	10,52	1,05	**5,33**	
Cochineal	AvL*	24,89	28,18	3,29	Ava*	42,68	42,57	-0,11	Avb*	10,21	10,61	0,40	**3,79**	
	L*1	44,99	56,45	11,46	a*1	30,87	38,01	7,14	b*1	25,16	31,13	5,97	**14,76**	*1,88*
	L*2	46,78	56,05	9,27	a*2	33,41	38,13	4,72	b*2	26,97	30,75	3,78	**11,07**	
	L*3	44,29	56,11	11,82	a*3	33,22	38,45	5,23	b*3	26,92	30,87	3,95	**13,52**	
Comb. 1	AvL*	45,35	56,20	10,85	Ava*	32,50	38,20	5,70	Avb*	26,35	30,92	4,57	**13,12**	
	L*1	42,53	53,44	10,91	a*1	28,43	36,61	8,18	b*1	23,76	32,1	8,34	**15,98**	2,26
	L*2	45,09	54,43	9,34	a*2	29,23	36,05	6,82	b*2	25,03	32,05	7,02	**13,53**	
	L*3	46,36	53,98	7,62	a*3	30,61	36,03	5,42	b*3	25,39	32,02	6,63	**11,46**	
Comb.2	AvL*	44,66	53,95	9,29	Ava*	29,42	36,23	6,81	Avb*	24,73	32,06	7,33	**13,66**	
	L*1	30,2	32,46	2,26	a*1	46,71	46,79	0,08	b*1	3,33	7,88	4,55	**5,08**	*2,14*
	L*2	30,44	31,98	1,54	a*2	48,76	47,42	-1,34	b*2	4,97	7,27	2,3	**3,08**	
	L*3	27,05	32,77	5,72	a*3	44,44	47,46	3,02	b*3	3,87	7,35	3,48	**7,35**	
Comb. 3	AvL*	29,23	32,40	3,17	Ava*	46,64	47,22	0,59	Avb*	4,06	7,50	3,44	**5,17**	

B.2.12 Colourimeric measurements of samples treated with inhibitor G

		Blank	treated	ΔL*		Blank	treated	Δa*		Blank	treated	Δb*	ΔE	Standard deviation
	L*1	44,18	61,11	16,93	a*1	34,34	34,78	0,44	b*1	24,61	28,09	3,48	**17,29**	*0,57*
	L*2	44,29	60,28	15,99	a*2	33,07	35,69	2,62	b*2	24,69	28,24	3,55	**16,59**	
	L*3	44,06	59,91	15,85	a*3	35,33	36,01	0,68	b*3	25,67	28,8	3,13	**16,17**	
Madder	AvL*	44,18	60,43	16,26	Ava*	34,25	35,49	1,25	Avb*	24,99	28,38	3,39	**16,68**	
	L*1	27,92	34,14	6,22	a*1	42,19	46,6	4,41	b*1	17,83	17,92	0,09	**7,63**	*1,15*
	L*2	29,28	33,92	4,64	a*2	43,5	47,15	3,65	b*2	17,79	18,18	0,39	**5,92**	
	L*3	29,37	33,49	4,12	a*3	43,95	47,49	3,54	b*3	18,15	18,58	0,43	**5,45**	
Brazilwood	AvL*	28,86	33,85	4,99	Ava*	43,21	47,08	3,87	Avb*	17,92	18,23	0,30	**6,33**	
	L*1	63,75	79,04	15,29	a*1	24,92	31,29	6,37	b*1	15,99	21,96	5,97	**17,61**	*1,23*
	L*2	66,93	79,16	12,23	a*2	23,85	31,13	7,28	b*2	15,8	21,19	5,39	**15,22**	
	L*3	66,01	79,24	13,23	a*3	24,4	31,18	6,78	b*3	15,85	21,43	5,58	**15,88**	
Safflower	AvL*	65,56	79,15	13,58	Ava*	24,39	31,2	6,81	Avb*	15,88	21,53	5,65	**16,23**	
	L*1	24,85	30,07	5,22	a*1	43,56	44,38	0,82	b*1	10,85	10,6	-0,25	**5,29**	*0,82*
	L*2	26,14	30,44	4,3	a*2	44,26	44,53	0,27	b*2	10,32	10,66	0,34	**4,32**	
	L*3	23,68	28,82	5,14	a*3	40,22	43,1	2,88	b*3	9,47	10,32	0,85	**5,95**	
Cochineal	AvL*	24,89	29,78	4,89	Ava*	42,68	44,00	1,32	Avb*	10,21	10,53	0,31	**5,19**	
	L*1	44,99	57,38	12,39	a*1	30,87	35,55	4,68	b*1	25,16	31,96	6,8	**14,89**	*1,92*
	L*2	46,78	57,1	10,32	a*2	33,41	35,49	2,08	b*2	26,97	30,45	3,48	**11,09**	
	L*3	44,29	57,57	13,28	a*3	33,22	34,04	0,82	b*3	26,92	29,31	2,39	**13,52**	
Comb. 1	AvL*	45,35	57,35	12,00	Ava*	32,50	35,03	2,53	Avb*	26,35	30,57	4,22	**13,16**	
	L*1	42,53	50,79	8,26	a*1	28,43	36,65	8,22	b*1	23,76	29,95	6,19	**13,20**	*2,09*
	L*2	45,09	51,28	6,19	a*2	29,23	36,63	7,4	b*2	25,03	30,19	5,16	**10,94**	
	L*3	46,36	51,98	5,62	a*3	30,61	36	5,39	b*3	25,39	29,95	4,56	**9,02**	
Comb.2	AvL*	44,66	51,35	6,69	Ava*	29,42	36,43	7,00	Avb*	24,73	30,03	5,30	**11,05**	
	L*1	30,2	30,69	0,49	a*1	46,71	50,55	3,84	b*1	3,33	10,74	7,41	**8,36**	*1,94*
	L*2	30,44	31,17	0,73	a*2	48,76	51,04	2,28	b*2	4,97	10,6	5,63	**6,12**	
	L*3	27,05	30,67	3,62	a*3	44,44	51,37	6,93	b*3	3,87	10,06	6,19	**9,97**	
Comb. 3	AvL*	29,23	30,84	1,61	Ava*	46,64	50,99	4,35	Avb*	4,06	10,47	6,41	**8,15**	

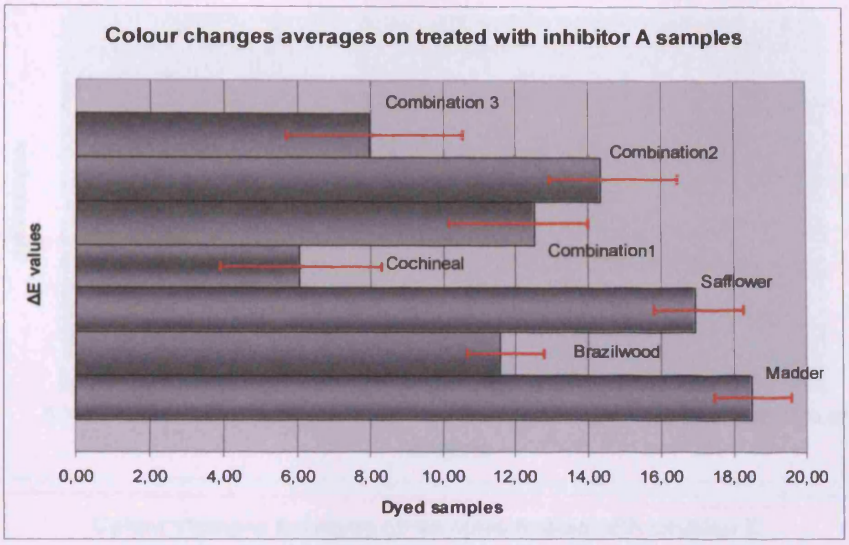
B.2.13 Colourimetric measurements treated with inhibitor H

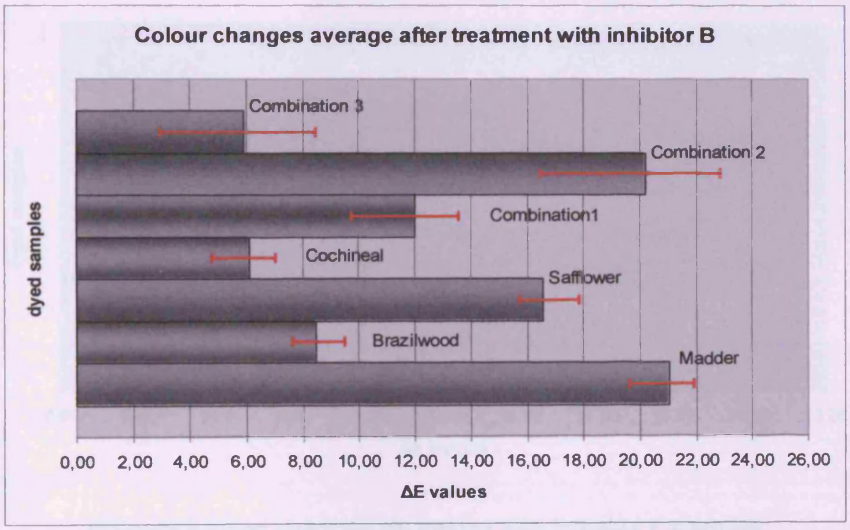
		Blank	treated	ΔL		Blank	treated	Δa		Blank	treated	Δb	ΔE	Standard deviation
	L*1	44,18	53,46	9,28	a*1	34,34	43,61	9,27	b*1	24,61	30,86	6,25	**14,53**	*4,18*
	L*2	44,29	53,92	9,63	a*2	33,07	43,85	10,78	b*2	24,69	39,91	15,22	**20,99**	
	L*3	44,06	53,87	9,81	a*3	35,33	42,64	7,31	b*3	25,67	30,5	4,83	**13,15**	
Madder	AvL*	44,18	53,75	9,57	Ava*	34,25	43,37	9,12	Avb*	24,99	33,76	8,77	**16,22**	
	L*1	27,92	34,88	6,96	a*1	42,19	45,53	3,34	b*1	17,83	18,23	0,4	**7,73**	*0,61*
	L*2	29,28	35,49	6,21	a*2	43,5	45,81	2,31	b*2	17,79	18,65	0,86	**6,68**	
	L*3	29,37	35,64	6,27	a*3	43,95	46,18	2,23	b*3	18,15	18,55	0,4	**6,67**	
Brazilwood	AvL*	28,86	35,34	6,48	Ava*	43,21	45,84	2,63	Avb*	17,92	18,48	0,55	**7,03**	
	L*1	63,75	78,23	14,48	a*1	24,92	32,03	7,11	b*1	15,99	23,12	7,13	**17,64**	*0,74*
	L*2	66,93	78,35	11,42	a*2	23,85	32,9	9,05	b*2	15,8	22,9	7,1	**16,21**	
	L*3	66,01	78,02	12,01	a*3	24,4	32,86	8,46	b*3	15,85	23,62	7,77	**16,62**	
Safflower	AvL*	65,56	78,20	12,64	Ava*	24,39	32,60	8,21	Avb*	15,88	23,21	7,33	**16,82**	
	L*1	24,85	29,71	4,86	a*1	43,56	41,77	-1,79	b*1	10,85	9,2	-1,65	**5,44**	*0,57*
	L*2	26,14	28,86	2,72	a*2	44,26	40	-4,26	b*2	10,32	8,63	-1,69	**5,33**	
	L*3	23,68	29,84	6,16	a*3	40,22	41,8	1,58	b*3	9,47	9,07	-0,4	**6,37**	
Cochineal	AvL*	24,89	29,47	4,58	Ava*	42,68	41,19	-1,49	Avb*	10,21	8,97	-1,25	**5,71**	
	L*1	44,99	54,8	9,81	a*1	30,87	39,21	8,34	b*1	25,16	31,23	6,07	**14,24**	*1,77*
	L*2	46,78	55,35	8,57	a*2	33,41	38,46	5,05	b*2	26,97	30,93	3,96	**10,71**	
	L*3	44,29	54,79	10,5	a*3	33,22	39,03	5,81	b*3	26,92	31,07	4,15	**12,70**	
Comb. 1	AvL*	45,35	54,98	9,62	Ava*	32,5	38,9	6,4	Avb*	26,35	31,07	4,72	**12,55**	
	L*1	42,53	53,68	11,15	a*1	28,43	37,34	8,91	b*1	23,76	31,89	8,13	**16,43**	*2,85*
	L*2	45,09	50,57	5,48	a*2	29,23	38,51	9,28	b*2	25,03	30,94	5,91	**12,29**	
	L*3	46,36	52,47	6,11	a*3	30,61	37,46	6,85	b*3	25,39	31,38	5,99	**10,96**	
Comb.2	AvL*	44,66	52,24	7,58	Ava*	29,42333	37,77	8,35	Avb*	24,73	31,40	6,68	**13,23**	
	L*1	30,2	32,43	2,23	a*1	46,71	49,5	2,79	b*1	3,33	7	3,67	**5,12**	*2,21*
	L*2	30,44	33,57	3,13	a*2	48,76	49,37	0,61	b*2	4,97	6,36	1,39	**3,48**	
	L*3	27,05	33,47	6,42	a*3	44,44	48,27	3,83	b*3	3,87	6,25	2,38	**7,85**	
Comb. 3	AvL*	29,23	33,16	3,93	Ava*	46,64	49,05	2,41	Avb*	4,06	6,54	2,48	**5,48**	

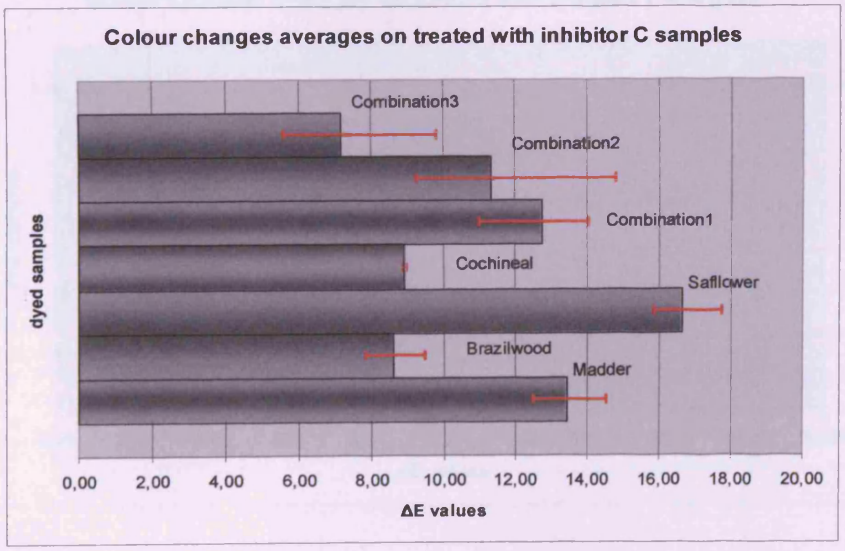
B.2.14 Colourimetric measurements of samples treated with inhibitor I

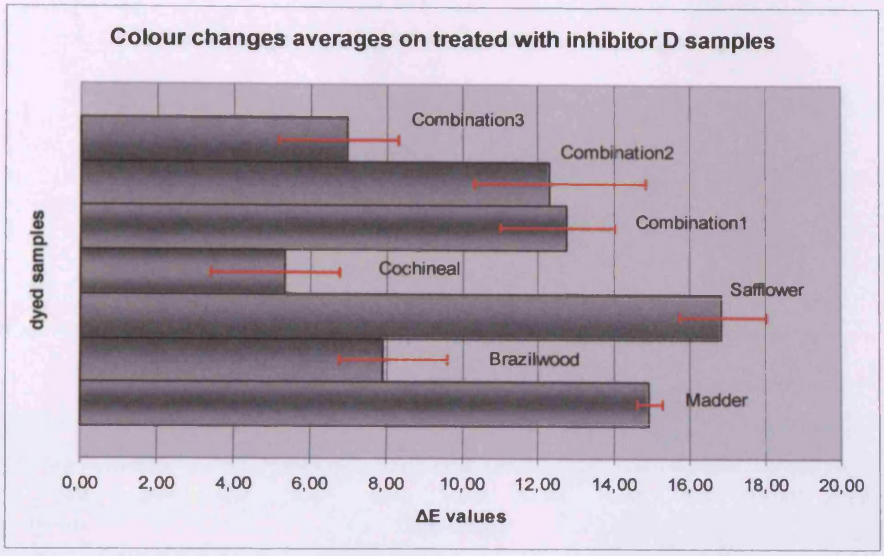
		Blank	treated	ΔL		Blank	treated	Δa		Blank	treated	Δb	ΔE	Standard deviation
	L*1	44,18	52,62	8,44	a*1	34,34	34,7	0,36	b*1	24,61	32,37	7,76	**11,47**	*4,90*
	L*2	44,29	63,73	19,44	a*2	33,07	33,86	0,79	b*2	24,69	31,83	7,14	**20,72**	
	L*3	44,06	62,04	17,98	a*3	35,33	34,46	-0,87	b*3	25,67	31,38	5,71	**18,88**	
Madder	AvL*	44,18	59,46	15,29	Ava*	34,25	34,34	0,09	Avb*	24,99	31,86	6,87	**17,03**	
	L*1	27,92	35,39	7,47	a*1	42,19	47,34	5,15	b*1	17,83	17,92	0,09	**9,07**	*1,17*
	L*2	29,28	35,36	6,08	a*2	43,5	47,37	3,87	b*2	17,79	17,81	0,02	**7,21**	
	L*3	29,37	35,23	5,86	a*3	43,95	47,65	3,7	b*3	18,15	18,25	0,1	**6,93**	
Brazilwood	AvL*	28,86	35,33	6,47	Ava*	43,21	47,45	4,24	Avb*	17,92	17,99	0,07	**7,74**	
	L*1	63,75	78,5	14,75	a*1	24,92	33,42	8,5	b*1	15,99	22,16	6,17	**18,11**	*0,91*
	L*2	66,93	78,5	11,57	a*2	23,85	32,72	8,87	b*2	15,8	23,36	7,56	**16,42**	
	L*3	66,01	78,51	12,5	a*3	24,4	33,51	9,11	b*3	15,85	22,12	6,27	**16,69**	
Safflower	AvL*	65,56	78,50	12,94	Ava*	24,39	33,22	8,83	Avb*	15,88	22,55	6,67	**17,07**	
	L*1	24,85	30,56	5,71	a*1	43,56	44,94	1,38	b*1	10,85	9,64	-1,21	**6,00**	*1,56*
	L*2	26,14	30,3	4,16	a*2	44,26	43,65	-0,61	b*2	10,32	9,21	-1,11	**4,35**	
	L*3	23,68	30,3	6,62	a*3	40,22	43,65	3,43	b*3	9,47	9,21	-0,26	**7,46**	
Cochineal	AvL*	24,89	30,39	5,496667	Ava*	42,68	44,08	1,40	Avb*	10,21	9,35	-0,86	**5,94**	
	L*1	44,99	56,91	11,92	a*1	30,87	36,44	5,57	b*1	25,16	29,3	4,14	**13,79**	*1,66*
	L*2	46,78	56,11	9,33	a*2	33,41	37,81	4,4	b*2	26,97	29,25	2,28	**10,56**	
	L*3	44,29	56,17	11,88	a*3	33,22	37,47	4,25	b*3	26,92	29,32	2,4	**12,84**	
Comb. 1	AvL*	45,35	56,40	11,04	Ava*	32,5	37,24	4,74	Avb*	26,35	29,29	2,94	**12,40**	
	L*1	42,53	56,03	13,5	a*1	28,43	30,94	2,51	b*1	23,76	28,74	4,98	**14,61**	*1,90*
	L*2	45,09	56,31	11,22	a*2	29,23	30,89	1,66	b*2	25,03	28,88	3,85	**11,98**	
	L*3	46,36	56,26	9,9	a*3	30,61	32,05	1,44	b*3	25,39	29,76	4,37	**10,92**	
Comb.2	AvL*	44,66	56,2	11,54	Ava*	29,42	31,29	1,87	Avb*	24,73	29,13	4,40	**12,50**	
	L*1	30,2	33,65	3,45	a*1	46,71	49,41	2,7	b*1	3,33	5,34	2,01	**4,82**	*2,43*
	L*2	30,44	33,5	3,06	a*2	48,76	49,73	0,97	b*2	4,97	5,71	0,74	**3,29**	
Comb. 3	L*3	27,05	33,16	6,11	a*3	44,44	49,39	4,95	b*3	3,87	5,57	1,7	**8,05**	
	AvL*	29,23	33,44	4,21	Ava*	46,64	49,51	2,87	Avb*	4,06	5,54	1,48	**5,39**	

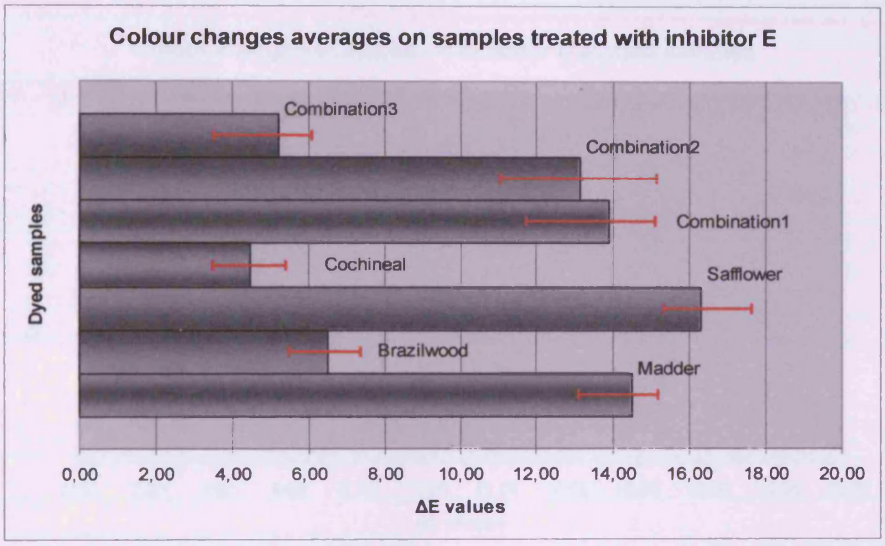
B.2.15 Graphs showing the colour changes averages on dyed with natural dyes and dye combinations silk fabric treated with selected inhibitors

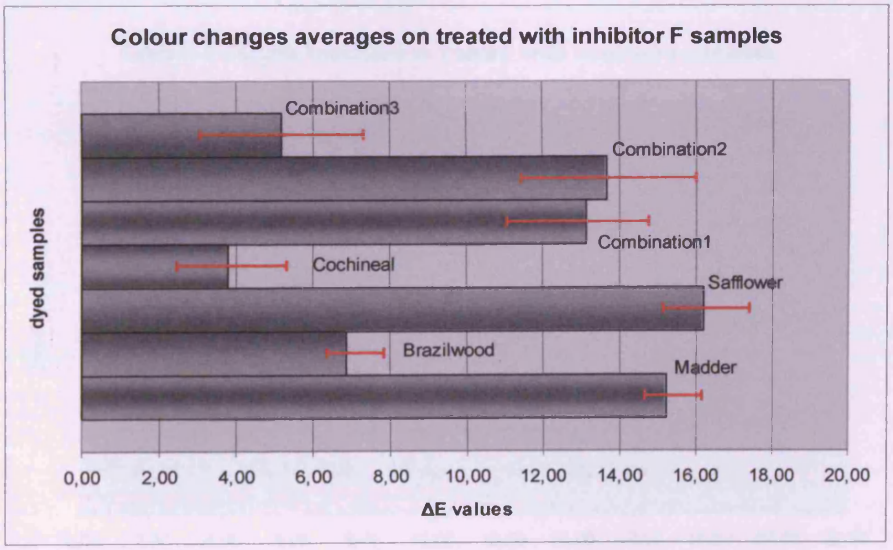


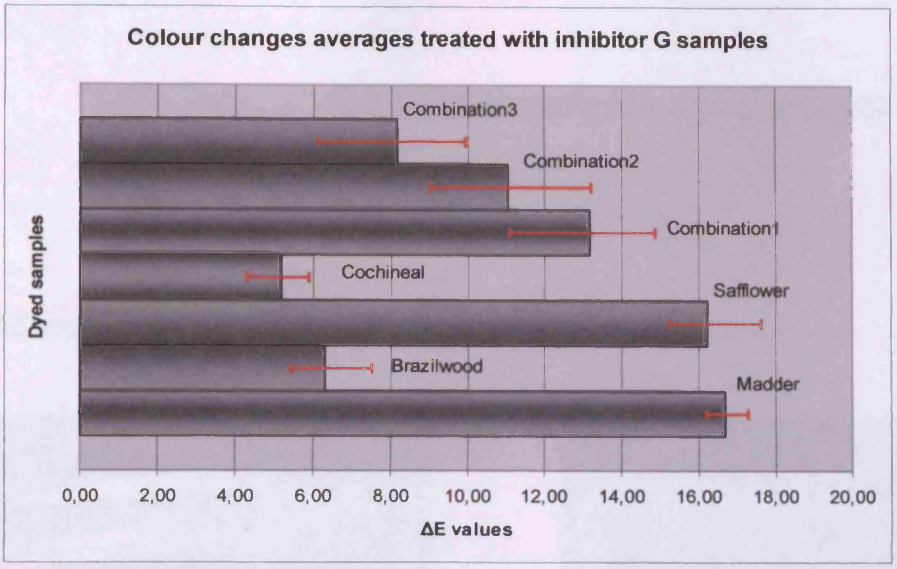


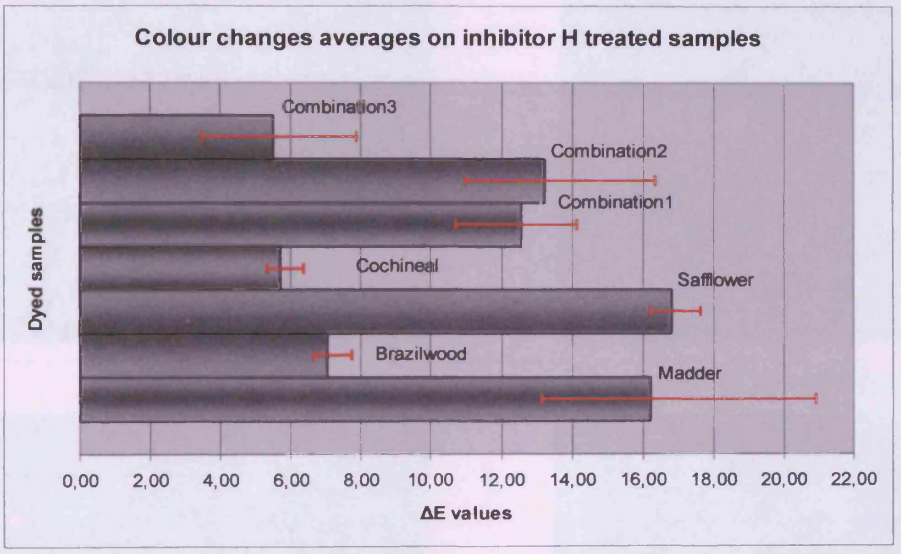


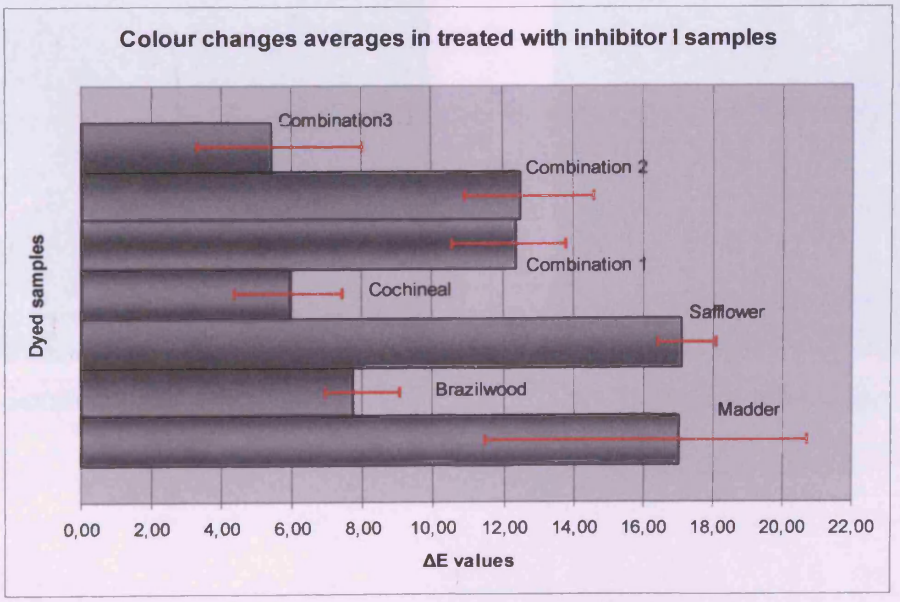

Colour changes averages on treated with inhibitor D samples
dyed samples
Combination3
Combination2
Combination1
Cochineal
Safflower
Brazilwood
Madder
0,00 2,00 4,00 6,00 8,00 10,00 12,00 14,00 16,00 18,00 20,00
ΔE values


Colour changes averages on samples treated with inhibitor E
Dyed samples
Combination3
Combination2
Combination1
Cochineal
Safflower
Brazilwood
Madder
0,00 2,00 4,00 6,00 8,00 10,00 12,00 14,00 16,00 18,00 20,00
ΔE values


Colour changes averages on treated with inhibitor F samples
dyed samples
Combination3
Combination2
Combination1
Cochineal
Safflower
Brazilwood
Madder
0,00 2,00 4,00 6,00 8,00 10,00 12,00 14,00 16,00 18,00 20,00
ΔE values


Colour changes averages treated with inhibitor G samples
Combination3
Combination2
Combination1
Cochineal
Safflower
Brazilwood
Madder
Dyed samples
0,00 2,00 4,00 6,00 8,00 10,00 12,00 14,00 16,00 18,00 20,00
ΔE values

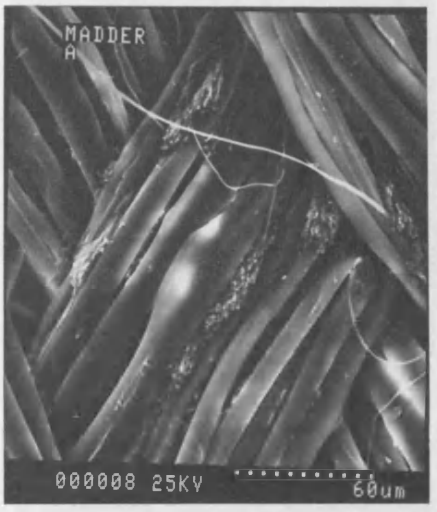

Colour changes averages on inhibitor H treated samples
Combination3
Combination2
Combination1
Cochineal
Safflower
Brazilwood
Madder
Dyed samples
0,00 2,00 4,00 6,00 8,00 10,00 12,00 14,00 16,00 18,00 20,00 22,00
ΔE values


Colour changes averages in treated with inhibitor I samples
Combination3
Combination 2
Combination 1
Cochineal
Safflower
Brazilwood
Madder
Dyed samples
0,00 2,00 4,00 6,00 8,00 10,00 12,00 14,00 16,00 18,00 20,00 22,00
ΔE values

B.3 SEM investigation of the treated samples

B.3.1 Samples dyed with madder and treated with inhibitors

Blank sample ×500



Sample treated with inhibitor A×500

Sample treated with inhibitor B×500

Sample treated with inhibitor C×500

Sample treated with inhibitor D×500

Sample treated with inhibitor E×100

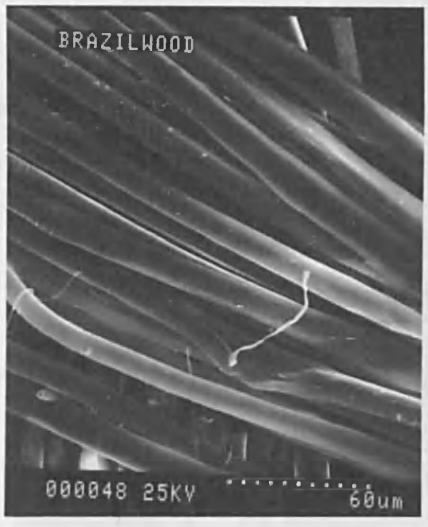
Sample treated with inhibitor F×500

Sample treated with inhibitor G×500

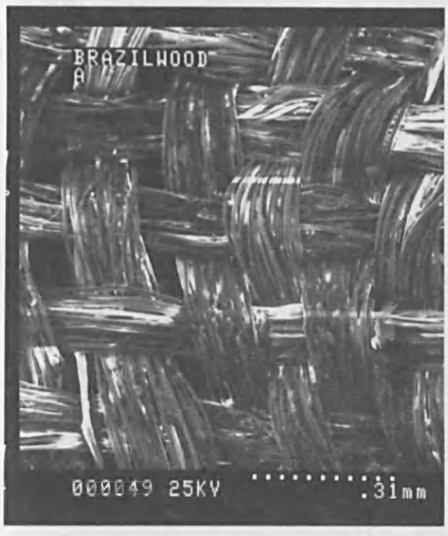
Sample treated with inhibitor H×500

Sample treated with inhibitor I×500

B.3.2 Sample dyed with Brazilwood and treated with inhibitors



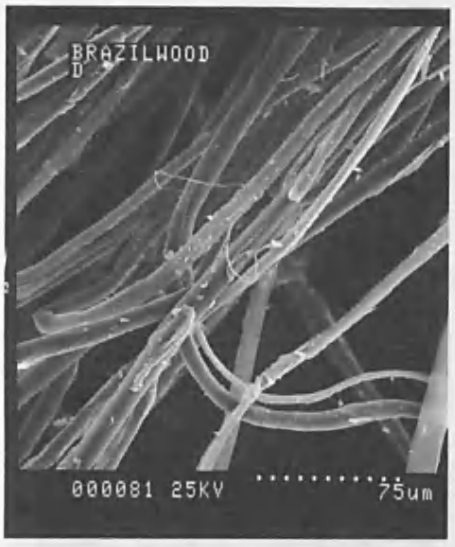
Blank sample ×500



Sample treated with inhibitor A×100

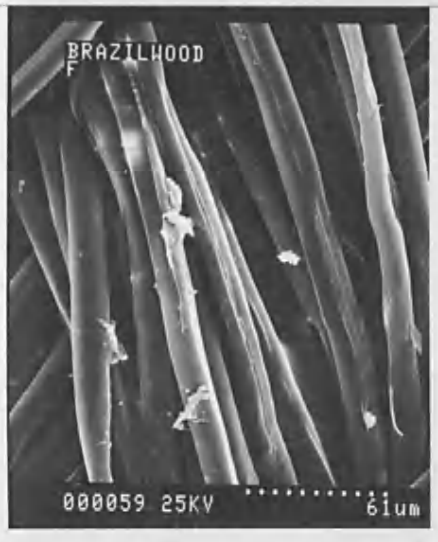
Sample treated with inhibitor B×500

Sample treated with inhibitor C×500



Sample treated with inhibitor D×400

Sample treated with inhibitor E×500



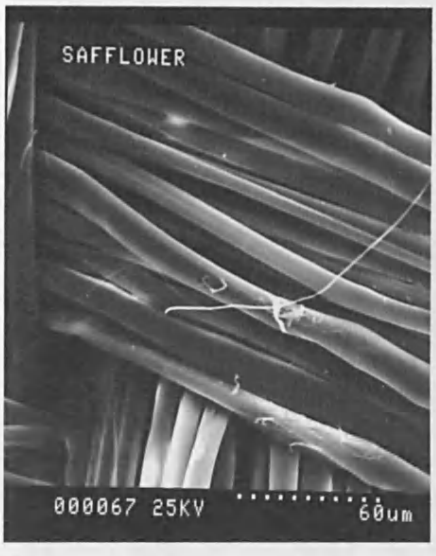
Sample treated with inhibitor F×500

Sample treated with inhibitor G×500

Sample treated with inhibitor H×500

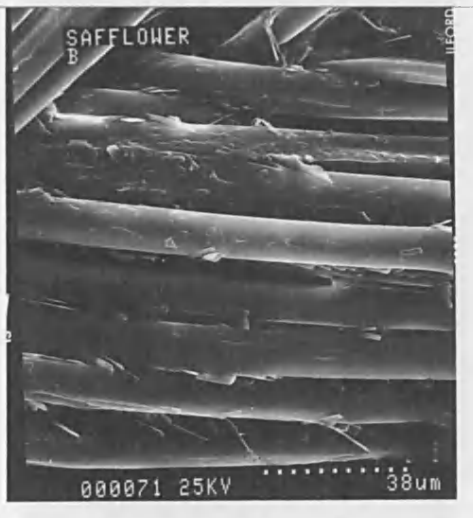
Sample treated with inhibitor I×500

B.3.3 Sample dyed with safflower and treated with inhibitors



Blank sample ×500

Sample treated with inhibitor A×500



Sample treated with inhibitor B×500

Sample treated with inhibitor C×500

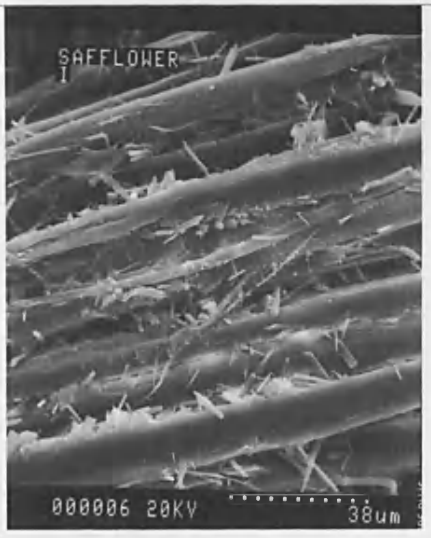
Sample treated with inhibitor D×500

Sample treated with inhibitor E×400

Sample treated with inhibitor F×500

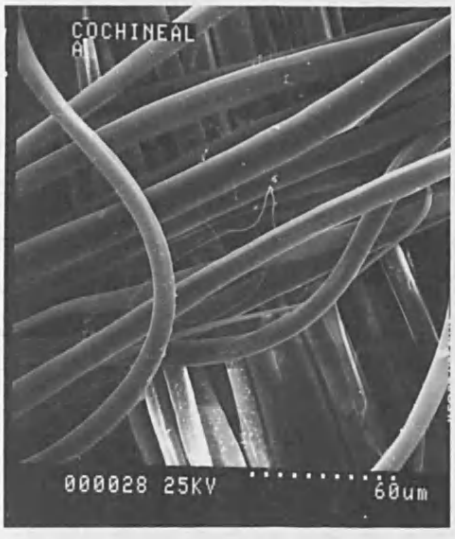
Sample treated with inhibitor G×500

Sample treated with inhibitor H×500

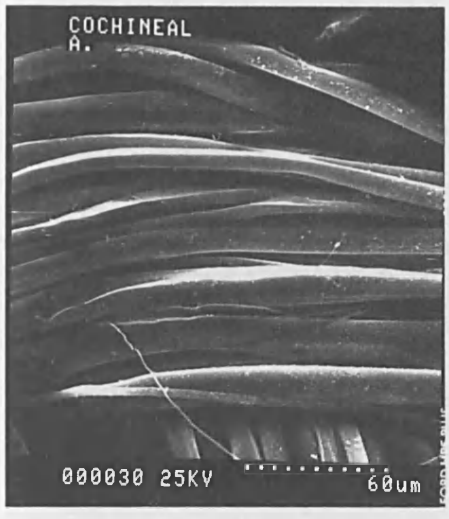


Sample treated with inhibitor I×500

B.3.4 Samples dyed with Cochineal and treated with inhibitors

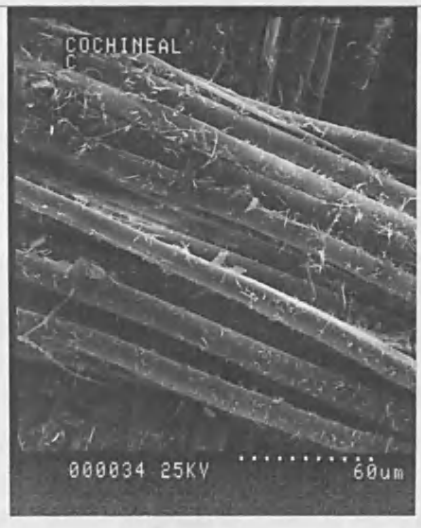


Blank sample ×500



Sample treated with inhibitor A×500

Sample treated with inhibitor B×500



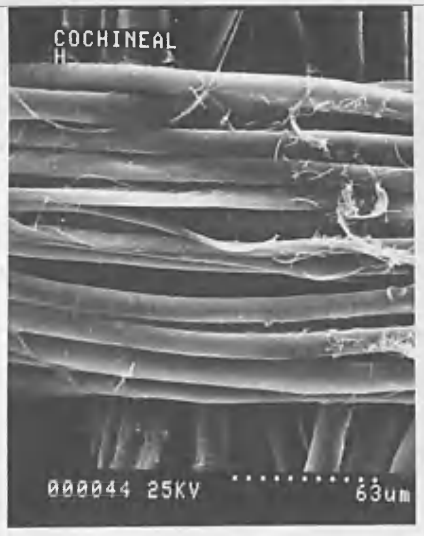
Sample treated with inhibitor C×500

Sample treated with inhibitor D×500

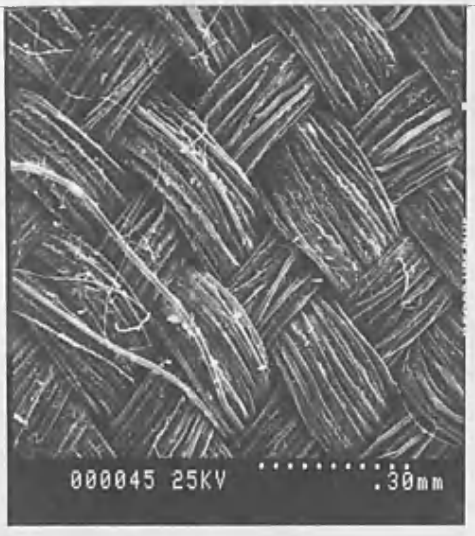
Sample treated with inhibitor E×500

Sample treated with inhibitor F×500

Sample treated with inhibitor G×500



Sample treated with inhibitor H×500



Sample treated with inhibitor I×100

B.4 Mechanical testing of silk fabric treated with inhibitors

B.4.1 Breaking strength and elongation of inhibitor treated silk fabric samples

		warp			weft			Overall change	
Inhibitors	*Treated samples*	*max load(N)*	*elong peak*	*elong%*	*max load (N)*	*elong peak*	*elong%*	*Av. Max load (N)*	*av elong%*
Blank sample	1	210,92	38,41	19,03	330,87	26,37	13,14	270,89	16,08
	2	210,97	36,91	18,28	312,09	25,00	12,47	261,53	15,38
	3	208,75	38,22	18,95	329,39	25,75	12,84	269,07	15,90
	4	209,14	37,05	18,32	315,01	25,37	12,64	262,07	15,48
	5	207,52	35,41	17,51	311,21	26,21	13,08	259,37	15,29
	Av	**209,46**	**37,20**	**18,42**	**319,71**	**25,74**	**12,83**	**264,59**	**15,63**
	STDEV	1,48	1,21	0,61	9,63	0,57	0,28	5,07	0,35
Inhibitor A	1	202,05	33,76	16,78	323,84	25,13	12,53	262,94	14,66
	2	200,27	33,79	16,81	303,88	23,72	11,83	252,08	14,32
	3	209,93	36,32	18,03	323,94	26,42	13,18	266,94	15,61
	4	212,59	36,47	18,15	309,36	26,56	12,25	260,98	15,20
	5	207,38	36,24	18,03	325,71	25,67	12,81	266,55	15,42
	Av	**206,45**	**35,32**	**17,56**	**317,35**	**25,50**	**12,52**	**261,90**	**15,04**
	STDEV	5,20	1,41	0,70	10,01	1,15	0,52	6,03	0,54
	change%	-1,44		-4,65	-0,74		-2,43	-1,.2	-3,73
Inhibitor B	1	202,76	36,16	17,91	309,88	22,94	11,43	256,32	14,67
	2	196,04	33,72	16,71	312,30	22,02	11,38	254,17	14,05
	3	204,75	37,01	18,30	315,75	23,20	11,57	260,25	14,93
	4	200,49	34,82	17,26	315,86	23,00	11,49	258,17	14,38
	5	196,44	29,11	14,46	315,77	23,63	11,78	256,10	13,12
	Av	**200,10**	**34,17**	**16,93**	**313,91**	**22,96**	**11,53**	**257,01**	**14,23**
	STDEV	3,83	3,09	1,51	2,72	0,59	0,16	2,30	0,70
	change%	-4,47		-8,09	-1,81		-10,15	2,87	-8,93
Inhibitor C	1	196,46	30,99	15,38	322,40	23,67	11,80	259,43	13,59
	2	208,02	34,97	17,37	302,16	23,72	11,83	255,09	14,60
	3	206,14	35,77	17,72	324,98	23,48	11,71	265,56	14,71
	4	208,80	36,05	17,88	328,18	23,49	11,71	268,49	14,80
	5	211,56	36,21	17,97	314,21	25,42	12,67	262,89	15,32
	Av	**206,20**	**34,80**	**17,26**	**318,39**	**23,95**	**11,94**	**262,29**	**14,60**
	STDEV	5,78	2,18	1,08	10,44	0,82	0,41	5,23	0,63
	change%	-1,56		-6,27	-0,42		-6,93	0,87	-6,54
Inhibitor D	1	201,67	34,21	16,99	320,67	23,49	11,72	261,17	14,35
	2	191,00	29,96	14,91	321,33	24,19	12,07	256,16	13,49
	3	183,88	28,11	13,97	302,55	23,64	11,81	243,21	12,89
	4	165,25	23,07	11,47	317,00	20,88	10,41	241,12	10,94
	5	199,67	33,02	16,41	320,27	22,56	11,25	259,97	13,83
	Av	**188,30**	**29,67**	**14,75**	**316,36**	**22,95**	**11,45**	**252,33**	**13,10**
	STDEV	14,72	4,41	2,19	7,90	1,30	0,65	9,49	1,32
	change%	-10,10		-19,93	-1,05		-10,78	4,63	-16,17

Appendix B: Application of Inhibitors– Evaluation of Treatments

		warp			weft			Overall change	
Inhibitors	*Treated samples*	*Max load (N)*	*elong peak*	*elong%*	*Max load (N)*	*elong peak*	*elong%*	*Av. Max load (N)*	*av elong%*
Inhibitor E	1	211,53	36,53	18,13	327,26	28,38	14,16	269,40	16,15
	2	202,82	34,70	17,23	349,04	28,82	14,37	275,93	15,80
	3	204,41	35,04	17,40	317,72	27,24	13,58	261,06	15,49
	4	210,31	37,32	18,56	343,76	28,06	14,00	277,03	16,28
	5	199,67	28,15	13,95	345,72	26,36	13,17	272,70	13,56
	Av	**205,75**	**34,35**	**17,06**	**336,70**	**27,77**	**13,86**	**271,22**	**15,46**
	STDEV	5,04	3,62	1,82	13,54	0,97	0,48	6,42	1,10
	change%	-1,77		-7,40	5,31		7,96	2,51	-1,09
Inhibitor F	1	210,68	37,97	18,87	328,29	27,36	13,65	269,49	16,26
	2	209,51	37,24	18,50	348,03	25,63	12,79	278,77	15,64
	3	210,04	37,72	18,75	339,43	25,90	12,92	274,73	15,83
	4	206,11	37,57	18,65	355,21	28,48	14,21	280,66	16,43
	5	207,97	35,99	18,88	351,60	29,45	14,69	279,79	16,79
	Av	**208,86**	**37,30**	**18,73**	**344,51**	**27,36**	**13,65**	**276,69**	**16,19**
	STDEV	1,84	0,78	0,16	10,79	1,64	0,82	4,62	0,46
	change%	-0,28		1,69	7,76		6,37	4,57	3,61
Inhibitor G	1	192,93	32,51	16,14	341,02	26,79	13,36	266,97	14,75
	2	197,02	34,84	17,32	320,12	22,86	11,38	258,57	14,35
	3	197,66	33,66	16,74	320,03	21,68	10,80	258,85	13,77
	4	192,03	31,82	15,79	325,83	23,88	11,90	258,93	13,84
	5	197,80	33,95	16,85	313,15	23,75	11,85	255,47	14,35
	Av	**195,49**	**33,36**	**16,57**	**324,03**	**23,79**	**11,86**	**259,76**	**14,21**
	STDEV	2,78	1,19	0,60	10,51	1,89	0,95	4,28	0,41
	change%	-6,67		-10,05	1,35		-7,62	-1,82	-9,05
Inhibitor H	1	210,39	34,41	16,81	368,37	32,93	16,43	289,38	16,62
	2	193,46	29,83	14,61	345,54	25,44	12,72	269,50	13,66
	3	213,26	33,93	16,62	345,24	26,89	13,41	279,25	15,02
	4	201,35	30,84	15,04	330,66	27,14	13,55	266,00	14,30
	5	201,38	29,58	14,47	362,63	28,63	14,30	282,00	14,39
	Av	**203,97**	**31,72**	**15,51**	**350,49**	**28,21**	**14,08**	**277,23**	**14,80**
	STDEV	7,93	2,29	1,12	15,10	2,87	1,43	9,49	1,13
	change%	-2,62		-15,80	9,62		9,73	4,78	-5,31
Inhibitor I	1	198,72	36,11	17,91	309,97	24,17	12,04	254,34	14,97
	2	194,58	34,90	17,31	327,31	23,75	11,86	260,95	14,58
	3	200,43	35,50	17,59	324,63	22,84	11,40	262,53	14,49
	4	198,30	35,98	17,85	331,64	28,64	14,31	264,97	16,08
	5	202,18	35,05	17,44	330,48	25,79	12,89	266,33	15,16
	Av	**198,84**	**35,51**	**17,62**	**324,81**	**25,04**	**12,50**	**261,82**	**15,06**
	STDEV	2,83	0,54	0,26	8,74	2,28	1,15	4,68	0,63
	change%	-5,07		-4,34	1,59		-2,61	1,04	-3,63

B.5 Removability

B.5.1 Weights of the non dyed silk fabric samples showing removability of the additives when treated through an Acetone solution

	Treated samples	Before	After application	After removal	% remnant of the additive on fabric	Standard deviation
Inhibitor A	A1	0,0985	0,1067	0,099	0,51	*0,26*
	A2	0,1013	0,111	0,1019	0,59	
	A3	0,1002	0,109	0,1012	1,00	
	Average				**0,70**	
Inhibitor B	B1	0,0996	0,1097	0,1005	0,90	*0,15*
	B2	0,0993	0,1088	0,1003	1,01	
	B3	0,0998	0,1098	0,101	1,20	
	Average				**1,04**	
Inhibitor D	D1	0,1007	0,1106	0,1018	1,09	*0,14*
	D2	0,1018	0,1128	0,1031	1,28	
	D3	0,103	0,1136	0,1044	1,36	
	Average				**1,24**	
Inhibitor E	E1	0,1036	0,1156	0,105	1,35	*0,06*
	E2	0,1035	0,1155	0,1048	1,26	
	E3	0,1016	0,1119	0,103	1,38	
	Average				**1,33**	
Inhibitor F	F1	0,1	0,1092	0,1013	1,30	*0,07*
	F2	0,1025	0,1129	0,1037	1,17	
	F3	0,0987	0,108	0,Q999	1,22	
					1,23	
Inhibitor G	G1	0,1013	0,1103	0,1028	1,48	*0,30*
	G2	0,1015	0,1107	0,1024	0,89	
	G3	0,1011	0,1096	0,1022	1,09	
	Average				**1,15**	

B.5.2 Weights of the non dyed silk fabric samples showing removability of the additives when treated through an Ethanol solution

	Treated samples	Before	After application	After removal	% remnant of the additive on fabric	Standard deviation
Inhibitor A	A1	0,099	0,106	0,0997	0,71	*0,31*
	A2	0,1014	0,1071	0,1027	1,28	
	A3	0,1007	0,106	0,1015	0,79	
	Average				**0,93**	
Inhibitor B	B1	0,1018	0,1104	0,1039	2,06	*0,47*
	B2	0,1012	0,109	0,1031	1,88	
	B3	0,1023	0,1085	0,1035	1,17	
	Average				**1,70**	
Inhibitor D	D1	0,0987	0,1056	0,1001	1,42	*0,38*
	D2	0,1028	0,111	0,1043	1,46	
	D3	0,1022	0,1088	0,103	0,78	
	Average				**1,22**	
Inhibitor G	G1	0,1068	0,1149	0,1076	0,75	*0,13*
	G2	0,1053	0,1134	0,1061	0,76	
	G3	0,1028	0,1111	0,1038	0,97	
	Average				**0,83**	

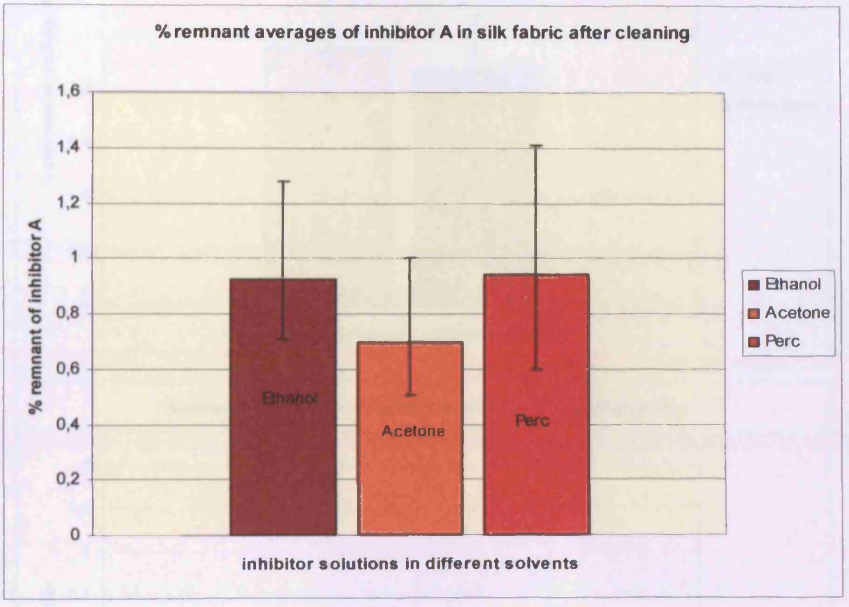
B.5.3 Weights of the non dyed silk fabric samples showing removability of the additives when treated through a Tetrachloroethylene solution

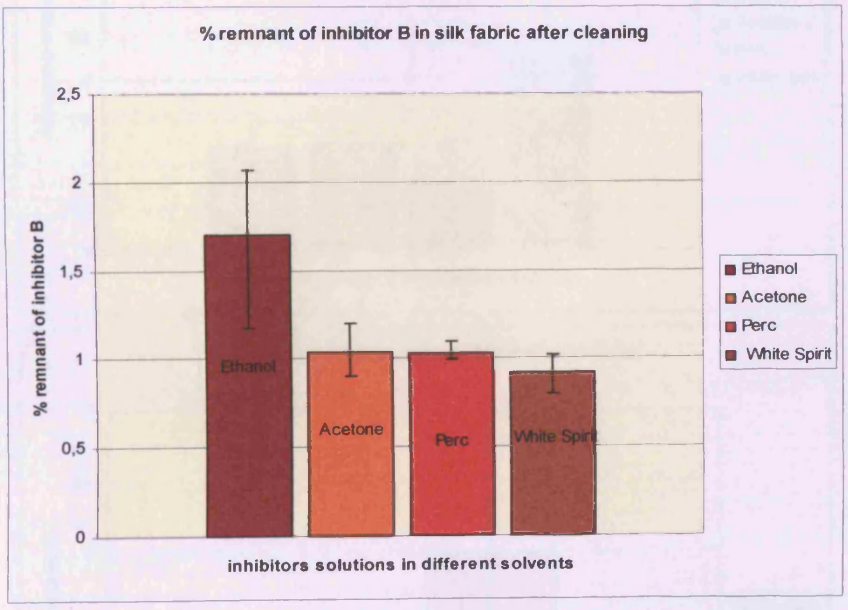
	Treated samples	Before	After application	After removal	% remnant of the additive on fabric	Standard deviation
Inhibitor A	A1	0,0994	0,1067	0,1008	1,41	*0,42*
	A2	0,1006	0,1071	0,1012	0,60	
	A3	0,0985	0,1049	0,0993	0,81	
	Average				**0,94**	
Inhibitor B	B1	0,1007	0,1078	0,1017	0,99	*0,06*
	B2	0,1008	0,1076	0,1019	1,09	
	B3	0,1006	0,1075	0,1016	0,99	
	Average				**1,03**	
Inhibitor C	C1	0,1009	0,1086	0,1015	0,59	*0,46*
	C2	0,1013	0,1101	0,1021	0,79	
	C3	0,1016	0,1097	0,1031	1,48	
	Average				**0,95**	
Inhibitor D	D1	0,1017	0,1115	0,1023	0,59	*0,45*
	D2	0,1025	0,112	0,103	0,49	
	D3	0,0992	0,1072	0,1005	1,31	
	Average				**0,80**	
Inhibitor E	E1	0,1005	0,1109	0,1029	2,39	*0,39*
	E2	0,1008	0,1138	0,1028	1,98	
	E3	0,1001	0,1109	0,1017	1,60	
	Average				**1,99**	
Inhibitor F	F1	0,0989	0,1088	0,1017	2,83	*0,39*
	F2	0,1008	0,1159	0,1043	3,47	
	F3	0,1013	0,1116	0,1041	2,76	
	Average				**3,02**	
Inhibitor G	G1	0,1013	0,1112	0,1057	4,34	*1,63*
	G2	0,0996	0,1065	0,1016	2,01	
	G3	0,0997	0,1084	0,1009	1,20	
	Average				**2,52**	
Inhibitor H	H1	0,0993	0,1109	0,1025	3,22	*0,48*
	H	0,0988	0,1115	0,1011	2,33	
	H3	0,1009	0,1201	0,1034	2,48	
	Average				**2,68**	
Inhibitor I	I1	0,0991	0,1099	0,1053	6,26	*2,05*
	I2	0,1024	0,1129	0,1058	3,32	
	I3	0,0994	0,1224	0,1017	2,31	
	Average				**3,96**	

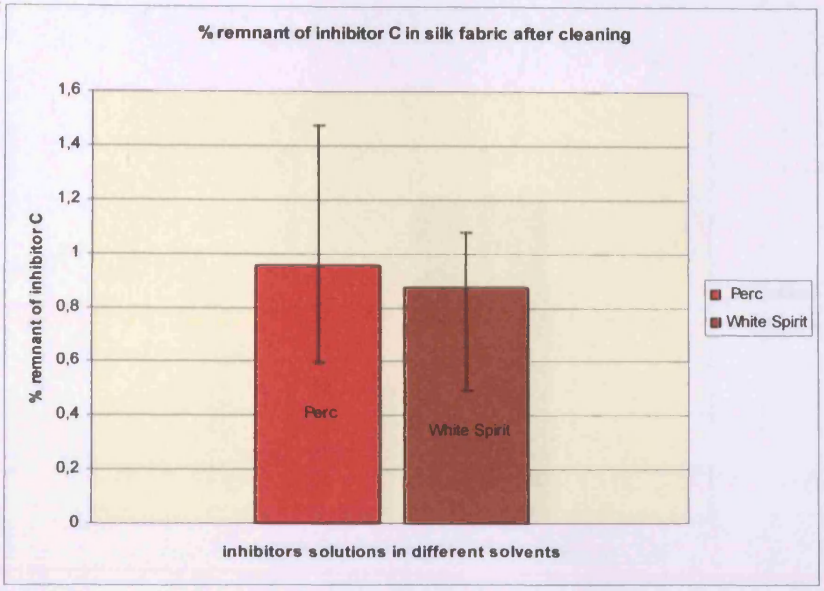
B.5.4 Weights of the non dyed silk fabric samples showing removability of the additives when treated through a White Spirit solution

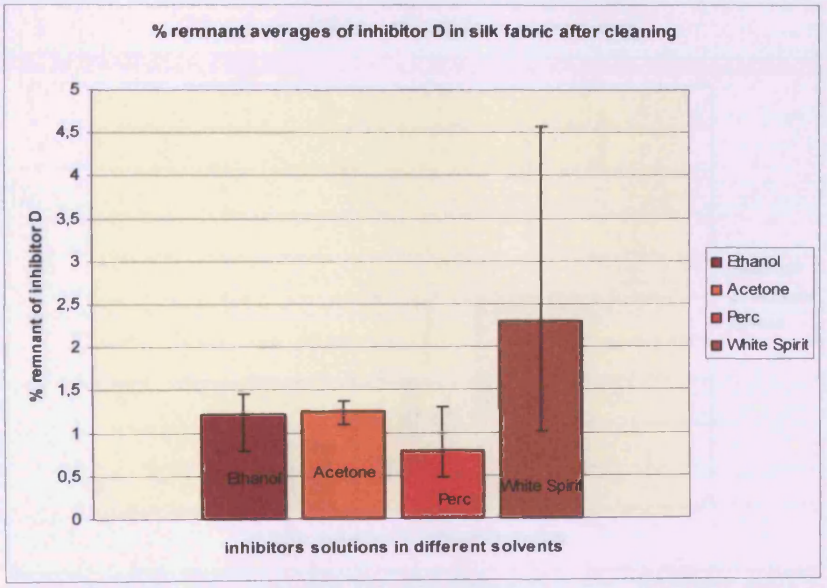
	Treated samples	Before	After application	After removal	% remnant of the additive on fabric	Standard deviation
Inhibitor B	B1	0,0983	0,1054	0,0993	1,02	*0,11*
	B2	0,1061	0,1134	0,1071	0,94	
	B3	0,0996	0,107	0,1004	0,80	
	Average				**0,92**	
Inhibitor C	C1	0,1014	0,1147	0,1025	1,08	*0,33*
	C2	0,0966	0,1019	0,0976	1,04	
	C3	0,1012	0,1043	0,1017	0,49	
	Average				**0,87**	
Inhibitor D	D1	0,0997	0,1051	0,1007	1,00	*1,97*
	D2	0,1055	0,1123	0,1069	1,33	
	D3	0,0986	0,1069	0,1031	4,56	
	Average				**2,30**	
Inhibitor I	I1	0,1017	0,108	0,1027	0,98	*0,05*
	I2	0,0994	0,1057	0,1004	1,01	
	I3	0,1015	0,1098	0,1026	1,08	
	Average				**1,02**	

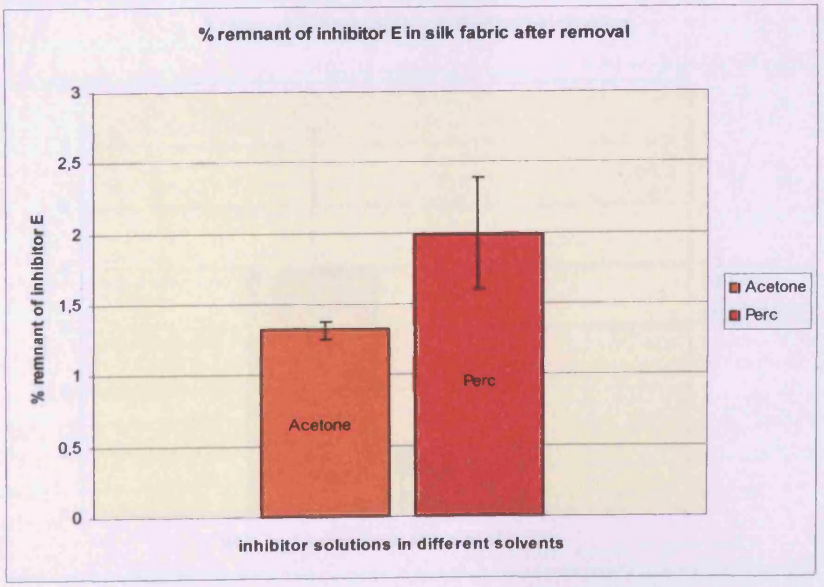
B.5.5 Graphs showing the % remnant averages of selected photodegradation inhibitors on silk fabric using different solvents

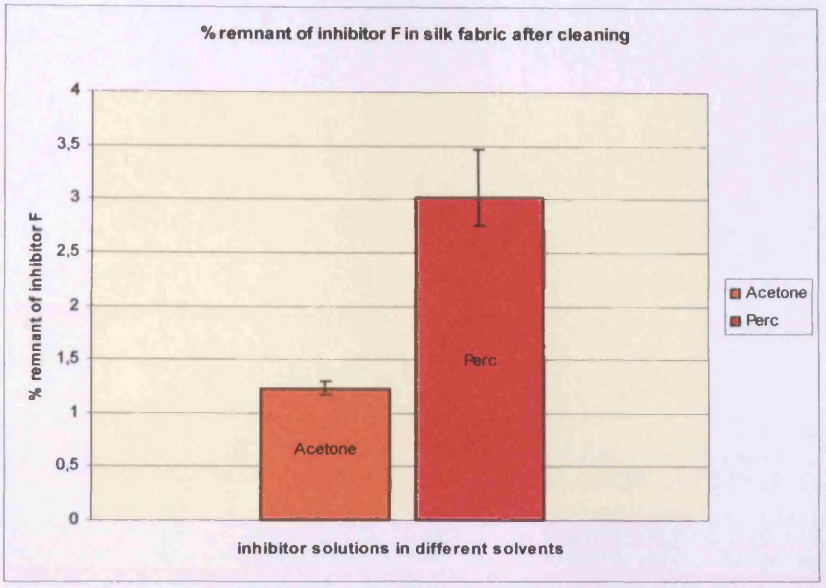


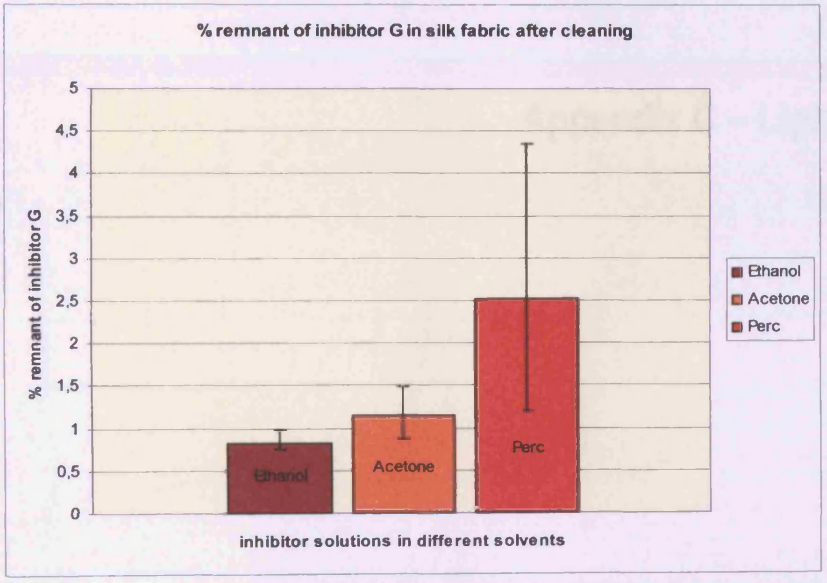


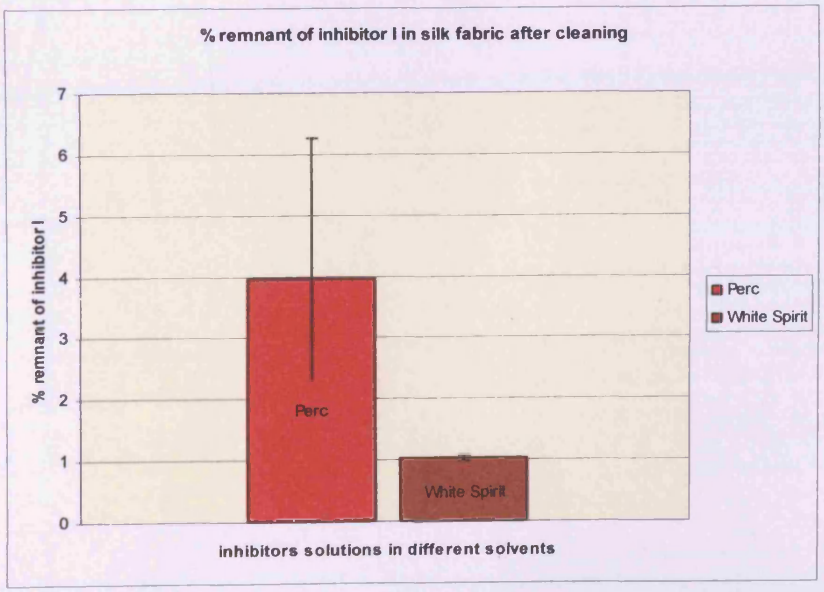

% remnant of inhibitor C in silk fabric after cleaning
% remnant of inhibitor C
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
Perc
White Spirit
Perc
White Spirit
inhibitors solutions in different solvents


% remnant averages of inhibitor D in silk fabric after cleaning
% remnant of inhibitor D
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
Ethanol
Acetone
Perc
White Spirit
Ethanol
Acetone
Perc
White Spirit
inhibitors solutions in different solvents


% remnant of inhibitor E in silk fabric after removal
% remnant of inhibitor E
3
2,5
2
1,5
1
0,5
0
Acetone
Perc
Acetone
Perc
inhibitor solutions in different solvents


% remnant of inhibitor F in silk fabric after cleaning
% remnant of inhibitor F
4
3,5
3
2,5
2
1,5
1
0,5
0
Acetone
Perc
Acetone
Perc
inhibitor solutions in different solvents


% remnant of inhibitor G in silk fabric after cleaning
% remnant of inhibitor G
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
Ethanol
Acetone
Perc
Ethanol
Acetone
Perc
inhibitor solutions in different solvents


% remnant of inhibitor I in silk fabric after cleaning
% remnant of inhibitor I
7
6
5
4
3
2
1
0
Perc
White Spirit
Perc
White Spirit
inhibitors solutions in different solvents

Appendix C – Light Fading Tests

C.1 Colourimetric measurements of samples exposed with the methods BS 1006:1990

C.1.1 Colourimetric measurements of Madder dyed samples exposed for 1439h

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	*Standard deviation*
	Blank sample												
L*1	53,57	63,4	9,83	a*1	44	37,44	-6,56	b*1	31,33	27,43	-3,9	12,44	*1,04*
L*2	53,65	63,43	9,78	a*2	44,65	37,78	-6,87	b*2	31,81	27,24	-4,57	12,80	
L*3	55,27	63,54	8,27	a*3	43,42	37,46	-5,96	b*3	31,34	27,64	-3,7	10,84	
L*Av	54,16	63,46	9,29	a*Av	44,02	37,56	-6,46	b*Av	31,49	27,44	-4,06	12,02	
	Inhibitor A												
L*1	59,88	63,47	3,59	a*1	38,9	37,49	-1,41	b*1	31,25	27,91	-3,34	5,10	*3,06*
L*2	57,09	64,13	7,04	a*2	41,62	36,83	-4,79	b*2	31,4	27,45	-3,95	9,39	
L*3	61,97	63,64	1,67	a*3	37,4	37,46	0,06	b*3	31,1	28,07	-3,03	3,46	
L*Av	59,65	63,75	4,10	a*Av	39,31	37,26	-2,05	b*Av	31,25	27,81	-3,44	5,73	
	Inhibitor B												
L*1	57,09	63,05	5,96	a*1	40,65	36,92	-3,73	b*1	31,47	28,36	-3,11	7,69	*0,81*
L*2	57,16	63,93	6,77	a*2	40,59	36,3	-4,29	b*2	31,31	28,13	-3,18	8,62	
L*3	57,87	63,82	5,95	a*3	39,59	36,56	-3,03	b*3	30,89	28,78	-2,11	7,00	
L*Av	57,37	63,60	6,23	a*Av	40,28	36,59	-3,68	b*Av	31,22	28,42	-2,8	7,76	
	Inhibitor C												
L*1	58,44	65,21	6,77	a*1	36,96	33,26	-3,7	b*1	28,18	25,68	-2,5	8,11	*1,59*
L*2	59	65,99	6,99	a*2	36,96	33,48	-3,48	b*2	28,07	25,99	-2,08	8,08	
L*3	60,06	64,75	4,69	a*3	35,43	33,88	-1,55	b*3	27,88	25,85	-2,03	5,34	
L*Av	59,17	65,32	6,15	a*Av	36,45	33,54	-2,91	b*Av	28,04	25,84	-2,20	7,15	
	Inhibitor D												
L*1	54,51	59,29	4,78	a*1	42,31	40,19	-2,12	b*1	30,54	29,01	-1,53	5,45	*1,37*
L*2	55,02	57,49	2,47	a*2	42,03	41,75	-0,28	b*2	30,82	29,25	-1,57	2,94	
L*3	55,02	59,5	4,48	a*3	41,8	39,96	-1,84	b*3	30,75	28,99	-1,76	5,15	
L*Av	54,85	58,76	3,91	a*Av	42,05	40,63	-1,41	b*Av	30,70	29,08	-1,62	4,46	

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	*Standard deviation*
	Inhibitor E												
L*1	53,46	59,11	5,65	a*1	44,28	41,83	-2,45	b*1	31,39	29,39	-2	6,47	*0,43*
L*2	54,59	61,24	6,65	a*2	42,88	40,21	-2,67	b*2	30,15	28,91	-1,24	7,27	
L*3	54,12	60,44	6,32	a*3	43,38	40,57	-2,81	b*3	30,29	28,44	-1,85	7,16	
L*Av	54,06	60,26	6,21	a*Av	43,51	40,87	-2,64	b*Av	30,61	28,91	-1,70	6,96	
	Inhibitor F												
L*1	57,3	62,79	5,49	a*1	40,02	37,48	-2,54	b*1	29,86	28,35	-1,51	6,23	*1,08*
L*2	57,9	63,3	5,4	a*2	39,85	37,53	-2,32	b*2	30,88	27,84	-3,04	6,62	
L*3	56,06	63,19	7,13	a*3	40,77	37,3	-3,47	b*3	30,16	27,84	-2,32	8,26	
L*Av	57,09	63,09	6,01	a*Av	40,21	37,44	-2,78	b*Av	30,3	28,01	-2,29	7,00	
	Inhibitor G												
L*1	54,25	61,86	7,61	a*1	42,54	38,26	-4,28	b*1	30,29	27,9	-2,39	9,05	*0,44*
L*2	54,6	62,06	7,46	a*2	42,56	37,74	-4,82	b*2	30,6	27,27	-3,33	9,49	
L*3	55,38	62,19	6,81	a*3	42,06	37,73	-4,33	b*3	30,42	27,44	-2,98	8,60	
L*Av	54,74	62,04	7,29	a*Av	42,39	37,91	-4,48	b*Av	30,44	27,54	-2,9	9,04	
	Inhibitor H												
L*1	55,35	64,49	9,14	a*1	41,46	35,27	-6,19	b*1	32,38	28,28	-4,1	11,78	*2,45*
L*2	56,56	63,88	7,32	a*2	40,93	35,73	-5,2	b*2	31,63	28,16	-3,47	9,63	
L*3	56,51	63,11	6,6	a*3	40,03	38,13	-1,9	b*3	30,63	30,07	-0,56	6,89	
L*Av	56,14	63,83	7,69	a*Av	40,81	36,38	-4,43	b*Av	31,55	28,84	-2,71	9,28	
	Inhibitor I												
L*1	60,6	62,92	2,32	a*1	37,36	37,04	-0,32	b*1	29,09	27,31	-1,78	2,94	*1,62*
L*2	61,35	64,02	2,67	a*2	35,6	35,3	-0,3	b*2	27,92	27	-0,92	2,84	
L*3	59,94	64,19	4,25	a*3	38,03	35,47	-2,56	b*3	29,56	26,76	-2,8	5,70	
L*Av	60,63	63,71	3,08	a*Av	37,00	35,94	-1,06	b*Av	28,86	27,02	-1,83	3,74	

C.1.2 Colourimetric measurements of Brazilwood dyed samples exposed for 295h

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	Standard deviation
	Blank sample												
L*1	35,89	47,43	11,54	a*1	46,64	33,34	-13,3	b*1	19,06	17,53	-1,53	17,67	0,68
L*2	36,48	47,46	10,98	a*2	46,94	33,82	-13,12	b*2	16,45	17,55	1,1	17,14	
L*3	36,15	47,95	11,8	a*3	47,41	33,32	-14,09	b*3	19,62	17,49	-2,13	18,50	
L*Av	36,17	47,61	11,44	a*Av	47,00	33,49	-13,50	b*Av	18,38	17,52	-0,85	17,72	
	A												
L*1	35,3	45,63	10,33	a*1	45,53	33,88	-11,65	b*1	20,2	17,56	-2,64	15,79	0,90
L*2	36,06	45,23	9,17	a*2	45,36	34,48	-10,88	b*2	20,12	17,92	-2,2	14,40	
L*3	35,65	47	11,35	a*3	45,42	34,26	-11,16	b*3	20,18	17,92	-2,26	16,08	
L*Av	35,67	45,95	10,28	a*Av	45,44	34,21	-11,23	b*Av	20,17	17,80	-2,37	15,41	
	B												
L*1	35,04	43,73	8,69	a*1	44,19	34,51	-9,68	b*1	19,55	17,24	-2,31	13,21	0,58
L*2	35,12	43,83	8,71	a*2	44,23	33,87	-10,36	b*2	19,48	17,03	-2,45	13,75	
L*3	35,77	44,61	8,84	a*3	44,7	33,64	-11,06	b*3	19,64	17,16	-2,48	14,37	
L*Av	35,31	44,06	8,75	a*Av	44,37	34,01	-10,37	b*Av	19,56	17,14	-2,41	13,78	
	C												
L*1	38,7	48,72	10,02	a*1	46,71	32,33	-14,38	b*1	19,77	16,55	-3,22	17,82	1,02
L*2	38,41	48,9	10,49	a*2	46,2	32,67	-13,53	b*2	19	16,87	-2,13	17,25	
L*3	37,59	49,33	11,74	a*3	46,43	31,62	-14,81	b*3	19,74	16,19	-3,55	19,23	
L*Av	38,23	48,98	10,75	a*Av	46,45	32,21	-14,24	b*Av	19,50	16,54	-2,97	18,09	
	D												
L*1	35,13	45,62	10,49	a*1	47,92	34,03	-13,89	b*1	19,66	17,83	-1,83	17,50	1,11
L*2	34,95	46,87	11,92	a*2	48,89	33,87	-15,02	b*2	20,06	17,84	-2,22	19,30	
L*3	34,45	47,34	12,89	a*3	48,01	33,48	-14,53	b*3	19,66	17,67	-1,99	19,53	
L*Av	34,84	46,61	11,77	a*Av	48,27	33,79	-14,48	b*Av	19,79	17,78	-2,01	18,77	

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	Standard deviation
	E												
L*1	35,51	46,77	11,26	a*1	46,2	34,06	-12,14	b*1	18,63	17,65	-0,98	16,59	2,14
L*2	35,29	43,33	8,04	a*2	46,22	36,53	-9,69	b*2	16,95	17,71	0,76	12,61	
L*3	35,92	45,9	9,98	a*3	47,49	35,17	-12,32	b*3	19,74	17,77	-1,97	15,98	
L*Av	35,57	45,33	9,76	a*Av	46,64	35,25	-11,38	b*Av	18,44	17,71	-0,73	15,01	
	F												
L*1	35,72	46,43	10,71	a*1	46,35	34,82	-11,53	b*1	19,17	17,6	-1,57	15,81	0,16
L*2	35,63	45,93	10,3	a*2	47,24	35,45	-11,79	b*2	19,64	17,76	-1,88	15,77	
L*3	34,73	46,92	12,19	a*3	44,41	34,82	-9,59	b*3	17,82	17,58	-0,24	15,51	
L*Av	35,36	46,43	11,07	a*Av	46,00	35,03	-10,97	b*Av	18,88	17,65	-1,23	15,63	
	G												
L*1	33,38	44,91	11,53	a*1	46,45	33,82	-12,63	b*1	19,16	18,17	-0,99	17,13	0,27
L*2	33,59	44,14	10,55	a*2	46,47	33,72	-12,75	b*2	19,52	17,89	-1,63	16,63	
L*3	32,48	44,29	11,81	a*3	45,26	33,46	-11,8	b*3	18,92	17,86	-1,06	16,73	
L*Av	33,15	44,45	11,30	a*Av	46,06	33,67	-12,39	b*Av	19,20	17,97	-1,23	16,81	
	H												
L*1	35,92	43,2	7,28	a*1	44,87	35,83	-9,04	b*1	20,05	17,67	-2,38	11,85	0,47
L*2	35,83	43,21	7,38	a*2	45,21	35,09	-10,12	b*2	20,13	17,59	-2,54	12,78	
L*3	36,53	43,78	7,25	a*3	45,24	35,36	-9,88	b*3	19,98	17,68	-2,3	12,47	
L*Av	36,09	43,40	7,30	a*Av	45,11	35,43	-9,68	b*Av	20,05	17,65	-2,41	12,36	
	I												
L*1	36,68	48,44	11,76	a*1	45,08	32,64	-12,44	b*1	17,32	15,99	-1,33	17,17	0,34
L*2	36,09	47,77	11,68	a*2	45,29	33,28	-12,01	b*2	17,6	16,44	-1,16	16,79	
L*3	36,71	47,63	10,92	a*3	45,24	32,93	-12,31	b*3	17,21	16,12	-1,09	16,49	
L*Av	36,49	47,95	11,45	a*Av	45,20	32,95	-12,25	b*Av	17,38	16,18	-1,19	16,82	

C.1.3 Colourimetric measurements of Safflower dyed samples exposed for 130h

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	*Standard deviation*
	Blank sample												
L*1	81,53	91,25	**9,72**	a*1	27,2	5,1	**-22,1**	b*1	19,32	15,69	**-3,63**	**24,41**	*2,51*
L*2	82,71	90,39	**7,68**	a*2	24,39	5,62	**-18,77**	b*2	17,76	16,57	**-1,19**	**20,32**	
L*3	81,25	91,01	**9,76**	a*3	27,61	4,92	**-22,69**	b*3	19,75	16,79	**-2,96**	**24,88**	
L*Av	81,83	90,88	**9,05**	a*Av	26,40	5,21	**-21,19**	b*Av	18,94	16,35	**-2,59**	**23,19**	
	A												
L*1	81,18	89,34	**8,16**	a*1	27,33	6,66	**-20,67**	b*1	21,87	18,22	**-3,65**	**22,52**	*2,00*
L*2	81,54	89,7	**8,16**	a*2	27,07	6,7	**-20,37**	b*2	21,14	18,26	**-2,88**	**22,13**	
L*3	80,84	91,33	**10,49**	a*3	28,11	5,41	**-22,7**	b*3	21,9	15,63	**-6,27**	**25,78**	
L*Av	81,19	90,12	**8,94**	a*Av	27,50	6,26	**-21,25**	b*Av	21,64	17,37	**-4,27**	**23,44**	
	B												
L*1	79,9	88,43	**8,53**	a*1	29,48	7,4	**-22,08**	b*1	22,93	21,16	**-1,77**	**23,74**	*0,62*
L*2	79,18	89,06	**9,88**	a*2	28,18	7,12	**-21,06**	b*2	23,43	20,6	**-2,83**	**23,43**	
L*3	79,93	89,03	**9,1**	a*3	29,6	6,95	**-22,65**	b*3	23,9	20,58	**-3,32**	**24,63**	
L*Av	79,67	88,84	**9,17**	a*Av	29,09	7,16	**-21,93**	b*Av	23,42	20,78	**-2,64**	**23,92**	
	C												
L*1	82,27	90,46	**8,19**	a*1	24,2	5,9	**-18,3**	b*1	24,83	20,17	**-4,66**	**20,58**	*1,04*
L*2	82,14	89,39	**7,25**	a*2	26,05	6,77	**-19,28**	b*2	23,2	21,62	**-1,58**	**20,66**	
L*3	81,91	90,22	**8,31**	a*3	26,39	5,98	**-20,41**	b*3	24,55	20,46	**-4,09**	**22,41**	
L*Av	82,11	90,02	**7,92**	a*Av	25,55	6,22	**-19,33**	b*Av	24,19	20,75	**-3,44**	**21,17**	
	D												
L*1	79,79	89,22	**9,43**	a*1	29,11	6,79	**-22,32**	b*1	24,24	19,66	**-4,58**	**24,66**	*2,23*
L*2	80,59	89,41	**8,82**	a*2	25,1	6,9	**-18,2**	b*2	22,95	19,82	**-3,13**	**20,47**	
L*3	80,28	89,15	**8,87**	a*3	28,36	6,69	**-21,67**	b*3	24,36	19,72	**-4,64**	**23,87**	
L*Av	80,22	89,26	**9,04**	a*Av	27,52	6,79	**-20,73**	b*Av	23,85	19,73	**-4,12**	**22,99**	

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	*Standard deviation*
	E												
L*1	79,73	90,02	**10,29**	a*1	29,2	5,89	**-23,31**	b*1	23,02	18,55	**-4,47**	**25,87**	*0,39*
L*2	80,04	89,31	**9,27**	a*2	28,33	5,58	**-22,75**	b*2	23,49	18,26	**-5,23**	**25,12**	
L*3	79,83	89,94	**10,11**	a*3	29,12	5,97	**-23,15**	b*3	23,09	18,68	**-4,41**	**25,64**	
L*Av	79,87	89,76	**9,89**	a*Av	28,88	5,81	**-23,07**	b*Av	23,20	18,50	**-4,70**	**25,54**	
	F												
L*1	80,25	88,75	**8,5**	a*1	28,76	6,82	**-21,94**	b*1	21,71	21	**-0,71**	**23,54**	*1,01*
L*2	80,44	88,42	**7,98**	a*2	27,43	6,81	**-20,62**	b*2	22,06	20,38	**-1,68**	**22,17**	
L*3	77,06	88,42	**11,36**	a*3	27,77	6,73	**-21,04**	b*3	23,39	20,04	**-3,35**	**24,14**	
L*Av	79,25	88,53	**9,28**	a*Av	27,99	6,79	**-21,20**	b*Av	22,39	20,47	**-1,91**	**23,22**	
	G												
L*1	79,04	89,43	**10,39**	a*1	30,86	6,69	**-24,17**	b*1	23,89	18,81	**-5,08**	**26,79**	*0,05*
L*2	78,74	89,09	**10,35**	a*2	31,86	7,48	**-24,38**	b*2	23,99	20,45	**-3,54**	**26,72**	
L*3	78,81	89,23	**10,42**	a*3	31,1	6,86	**-24,24**	b*3	24	19,97	**-4,03**	**26,69**	
L*Av	78,86	89,25	**10,39**	a*Av	31,27	7,01	**-24,26**	b*Av	23,96	19,74	**-4,22**	**26,73**	
	H												
L*1	79,37	88,5	**9,13**	a*1	30,04	6,8	**-23,24**	b*1	22,09	20,3	**-1,79**	**25,03**	*4,21*
L*2	79,51	88,1	**8,59**	a*2	29,41	7,42	**-21,99**	b*2	22,23	20,24	**-1,99**	**23,69**	
L*3	79,64	88,51	**8,87**	a*3	37,06	6,8	**-30,26**	b*3	21,43	20,26	**-1,17**	**31,55**	
L*Av	79,51	88,37	**8,86**	a*Av	32,17	7,01	**-25,16**	b*Av	21,92	20,27	**-1,65**	**26,73**	
	I												
L*1	79,1	89,62	**10,52**	a*1	30,74	3,76	**-26,98**	b*1	22,65	20,8	**-1,85**	**29,02**	*2,28*
L*2	78,36	90,7	**12,34**	a*2	31,63	2,71	**-28,92**	b*2	22,41	19,23	**-3,18**	**31,60**	
L*3	78,7	89,3	**10,6**	a*3	31,03	6,15	**-24,88**	b*3	21,91	21,18	**-0,73**	**27,05**	
L*Av	78,72	89,87	**11,15**	a*Av	31,13	4,21	**-26,93**	b*Av	22,32	20,40	**-1,92**	**29,21**	

C.1.4 Colourimetric measurements of Cochineal dyed samples exposed for 1231h

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	*Standard deviation*
	Blank sample												
L*1	29,33	36,47	7,14	a*1	44,78	43,31	-1,47	b*1	10,76	8,72	-2,04	7,19	*0,48*
L*2	29,89	37,45	7,56	a*2	44,53	43,67	-0,86	b*2	9,95	8,67	-1,28	7,72	
L*3	30,19	36,75	6,56	a*3	44,72	43,61	-1,11	b*3	10,09	8,92	-1,17	6,76	
L*Av	29,80	36,89	7,09	a*Av	44,68	43,53	-1,15	b*Av	10,27	8,77	-1,50	7,33	
	A												
L*1	31,34	36,23	4,89	a*1	44,55	42,84	-1,71	b*1	9,79	8,67	-1,12	4,67	*0,38*
L*2	30,55	35,82	5,27	a*2	43,23	42,77	-0,46	b*2	9,24	8,81	-0,43	5,31	
L*3	31,62	36,21	4,59	a*3	45,26	42,93	-2,33	b*3	10,26	8,82	-1,44	5,35	
L*Av	31,17	36,09	4,92	a*Av	44,35	42,85	-1,50	b*Av	9,76	8,77	-1,00	5,24	
	B												
L*1	30,41	36,37	5,96	a*1	44,02	44,45	0,43	b*1	10,24	9,97	-0,27	5,91	*0,63*
L*2	29,92	36,19	6,27	a*2	45,68	44,34	-1,34	b*2	11,18	9,88	-1,3	6,54	
L*3	30,51	37,49	6,98	a*3	44,59	43,6	-0,99	b*3	10,57	9,25	-1,32	7,17	
L*Av	30,28	36,68	6,40	a*Av	44,76	44,13	-0,63	b*Av	10,66	9,70	-0,96	6,51	
	C												
L*1	33,98	39,14	5,16	a*1	45,03	42,08	-2,95	b*1	9,45	7,32	-2,13	5,62	*0,07*
L*2	33,88	39,08	5,2	a*2	43,21	41,74	-1,47	b*2	8,31	7,14	-1,17	5,53	
L*3	33,78	38,16	4,38	a*3	44,99	41,78	-3,21	b*3	9,39	7,75	-1,64	5,67	
L*Av	33,88	38,79	4,91	a*Av	44,41	41,87	-2,54	b*Av	9,05	7,40	-1,65	5,77	
	D												
L*1	28,16	35,37	7,21	a*1	44,8	43,06	-1,74	b*1	10,14	8,72	-1,42	6,52	*0,69*
L*2	28,48	35,11	6,63	a*2	45,26	43,83	-1,43	b*2	10,4	9,06	-1,34	6,91	
L*3	28,22	35,98	7,76	a*3	44,65	43,95	-0,7	b*3	10,2	9,18	-1,02	7,86	
L*Av	28,29	35,49	7,20	a*Av	44,90	43,61	-1,29	b*Av	10,25	8,99	-1,26	7,42	

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	*Standard deviation*
	E												
L*1	29,29	34,49	5,2	a*1	43,41	42,92	-0,49	b*1	9,5	9,46	-0,04	3,70	*1,04*
L*2	29,26	34,24	4,98	a*2	43,83	42,6	-1,23	b*2	10,13	9,5	-0,63	5,17	
L*3	28,96	34,36	5,4	a*3	44,99	43,19	-1,8	b*3	9,83	9,54	-0,29	5,70	
L*Av	29,17	34,36	5,19	a*Av	44,08	42,90	-1,17	b*Av	9,82	9,50	-0,32	5,33	
	F												
L*1	30,47	36,79	6,32	a*1	46,37	41,84	-4,53	b*1	10,11	8,37	-1,74	6,47	*1,52*
L*2	30,7	35,72	5,02	a*2	46,1	41,13	-4,97	b*2	10,18	8,03	-2,15	7,38	
L*3	28,2	35,4	7,2	a*3	45,41	39,64	-5,77	b*3	9,99	7,98	-2,01	9,44	
L*Av	29,79	35,97	6,18	a*Av	45,96	40,87	-5,09	b*Av	10,09	8,13	-1,97	8,24	
	G												
L*1	30,75	36,49	5,74	a*1	44,91	42,25	-2,66	b*1	10,29	8,5	-1,79	5,95	*1,50*
L*2	29,31	36,77	7,46	a*2	46,17	43,3	-2,87	b*2	10,8	8,69	-2,11	8,27	
L*3	29,74	34,97	5,23	a*3	43,63	42,61	-1,02	b*3	9,99	8,8	-1,19	5,46	
L*Av	29,93	36,08	6,14	a*Av	44,90	42,72	-2,18	b*Av	10,36	8,66	-1,70	6,74	
	H												
L*1	29,45	35,07	5,62	a*1	42,08	40,83	-1,25	b*1	9,66	8,29	-1,37	5,53	*0,62*
L*2	29,59	35,42	5,83	a*2	42,39	41,1	-1,29	b*2	9,04	8,37	-0,67	6,01	
L*3	29,03	35,41	6,38	a*3	42,33	40,65	-1,68	b*3	9,59	8,12	-1,47	6,76	
L*Av	29,36	35,30	5,94	a*Av	42,27	40,86	-1,41	b*Av	9,43	8,26	-1,17	6,22	
	I												
L*1	31,91	37,05	5,14	a*1	43,89	38,5	-5,39	b*1	8,86	6,27	-2,59	7,89	*0,39*
L*2	31,26	37,58	6,32	a*2	44	40,11	-3,89	b*2	9,53	7,33	-2,2	7,74	
L*3	31,6	36,34	4,74	a*3	44,48	39,62	-4,86	b*3	8,84	6,6	-2,24	7,15	
L*Av	31,59	36,99	5,4	a*Av	44,12	39,41	-4,71	b*Av	9,08	6,73	-2,34	7,54	

C.1.5 Colourimetric measurements of Combination 1 dyed samples exposed for 371h

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	*Standard deviation*
	Blank sample												
L*1	54,56	60,66	6,1	a*1	38,45	36,25	-2,2	b*1	31,37	30,52	-0,85	6,54	*1,16*
L*2	55,89	60,14	4,25	a*2	37,56	37,34	-0,22	b*2	31,18	30,74	-0,44	4,28	
L*3	54,82	60,4	5,58	a*3	38,23	36,57	-1,66	b*3	31,31	30,59	-0,72	5,87	
L*Av	55,09	60,4	5,31	a*Av	38,08	36,72	-1,36	b*Av	31,29	30,62	-0,67	5,52	
	A												
L*1	60,02	64,84	4,82	a*1	34,32	33,4	-0,92	b*1	31,32	30,67	-0,65	4,95	*0,37*
L*2	59,13	64,1	4,97	a*2	35,1	33,66	-1,44	b*2	31,06	29,86	-1,2	5,31	
L*3	60,46	60,06	-0,4	a*3	34,15	29,99	-4,16	b*3	31,33	27,47	-3,86	5,69	
L*Av	59,87	63	3,13	a*Av	34,52	32,35	-2,17	b*Av	31,24	29,33	-1,90	4,26	
	B												
L*1	56,53	60,86	4,33	a*1	35,7	31,2	-4,5	b*1	31,2	30,3	-0,9	6,31	*1,25*
L*2	58,4	61,29	2,89	a*2	34,03	30,21	-3,82	b*2	30,21	29,99	-0,22	4,80	
L*3	56,57	61,79	5,22	a*3	35,65	30,57	-5,08	b*3	30,57	30,62	0,05	7,28	
L*Av	57,17	61,31	4,15	a*Av	35,13	30,66	-4,47	b*Av	30,66	30,30	-0,36	6,11	
	C												
L*1	57,81	56,65	-1,16	a*1	36,92	31,44	-5,48	b*1	29,39	25,22	-4,17	6,98	*0,63*
L*2	58,2	63,4	5,2	a*2	36,65	33,44	-3,21	b*2	29,99	27,71	-2,28	6,52	
L*3	57,42	62,26	4,84	a*3	36,91	34,31	-2,6	b*3	29,67	28,05	-1,62	5,73	
L*Av	57,81	60,77	2,96	a*Av	36,83	33,06	-3,76	b*Av	29,68	26,99	-2,69	5,49	
	D												
L*1	59,32	68,75	9,43	a*1	35,28	29,16	-6,12	b*1	31,41	29,27	-2,14	11,44	*1,50*
L*2	58,08	66,57	8,49	a*2	36,31	31,01	-5,3	b*2	30,87	29,47	-1,4	10,11	
L*3	59,85	67,35	7,5	a*3	34,69	31,05	-3,64	b*3	31,09	29,66	-1,43	8,46	
L*Av	59,08	67,56	8,47	a*Av	35,43	30,41	-5,02	b*Av	31,12	29,47	-1,66	9,99	

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	*Standard deviation*
	E												
L*1	55,29	62,69	7,4	a*1	37,25	35,37	-1,88	b*1	31,87	31,29	-0,58	7,66	*0,77*
L*2	55,77	62,1	6,33	a*2	36,83	36,18	-0,65	b*2	32,35	31,49	-0,86	6,42	
L*3	56,82	63,05	6,23	a*3	35,15	35,32	0,17	b*3	31,6	31,26	-0,34	6,24	
L*Av	55,96	62,61	6,65	a*Av	36,41	35,62	-0,79	b*Av	31,94	31,35	-0,59	6,73	
	F												
L*1	56,48	62,93	6,45	a*1	38,22	35,96	-2,26	b*1	31,42	30,77	-0,65	6,87	*0,99*
L*2	56,77	61,59	4,82	a*2	37,68	36,87	-0,81	b*2	31,14	31,03	-0,11	4,89	
L*3	57,24	62,92	5,68	a*3	37,85	35,89	-1,96	b*3	31,08	30,7	-0,38	6,02	
L*Av	56,83	62,48	5,65	a*Av	37,92	36,24	-1,68	b*Av	31,21	30,83	-0,38	5,91	
	G												
L*1	57,35	63,14	5,79	a*1	35,68	34,82	-0,86	b*1	30,15	30,05	-0,1	5,85	*0,25*
L*2	57,29	62,69	5,4	a*2	36,92	34,75	-2,17	b*2	30,9	29,73	-1,17	5,94	
L*3	57,41	63,29	5,88	a*3	36,32	34,16	-2,16	b*3	30,43	29,61	-0,82	6,32	
L*Av	57,35	63,04	5,69	a*Av	36,31	34,58	-1,73	b*Av	30,49	29,80	-0,70	5,99	
	H												
L*1	55,24	59,49	4,25	a*1	37,62	37,72	0,1	b*1	32,19	31,1	-1,09	4,39	*0,78*
L*2	55,48	60,61	5,13	a*2	38,14	37,5	-0,64	b*2	31,61	31,54	-0,07	5,17	
L*3	57,25	60,79	3,54	a*3	35,83	36,35	0,52	b*3	30,72	30,31	-0,41	3,60	
L*Av	55,99	60,30	4,31	a*Av	37,20	37,19	-0,01	b*Av	31,51	30,98	-0,52	4,34	
	I												
L*1	57,79	63,91	6,12	a*1	33,85	32,55	-1,3	b*1	26,71	27,35	0,64	6,29	*1,00*
L*2	56,82	64,52	7,7	a*2	34,67	31,74	-2,93	b*2	27,55	26,88	-0,67	8,27	
L*3	58,06	65,24	7,18	a*3	33,61	31,21	-2,4	b*3	26,49	26,37	-0,12	7,57	
L*Av	57,56	64,56	7,00	a*Av	34,04	31,83	-2,21	b*Av	26,92	26,87	-0,05	7,34	

C.1.6 Colourimetric measurements of Combination 2 dyed samples exposed for 400h

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	*Standard deviation*
	Blank sample												
L*1	57,75	60,63	2,88	a*1	35,93	36,44	0,51	b*1	32,16	30,61	-1,55	3,31	*0,57*
L*2	57,49	60,74	3,25	a*2	36,27	35,98	-0,29	b*2	31,44	30,16	-1,28	3,50	
L*3	57,66	60,1	2,44	a*3	39,42	36,94	-2,48	b*3	33,05	30,38	-2,67	4,39	
L*Av	57,63	60,49	2,86	a*Av	37,21	36,45	-0,75	b*Av	32,22	30,38	-1,83	3,48	
	A												
L*1	59,28	63,99	4,71	a*1	31,55	31,22	-0,33	b*1	32,33	31,58	-0,75	4,78	*0,50*
L*2	59,74	64,98	5,24	a*2	31,18	30,87	-0,31	b*2	32,41	30,1	-2,31	5,73	
L*3	58,68	64,07	5,39	a*3	31,91	31,41	-0,5	b*3	32,23	31,23	-1	5,50	
L*Av	59,23	64,35	5,11	a*Av	31,55	31,17	-0,38	b*Av	32,32	30,97	-1,35	5,30	
	B												
L*1	58,69	61,6	2,91	a*1	30,82	32,73	1,91	b*1	31,2	30,71	-0,49	3,52	*0,53*
L*2	59,54	63,27	3,73	a*2	30,14	31,99	1,85	b*2	31,02	30,37	-0,65	4,21	
L*3	58,37	62,64	4,27	a*3	31,14	32,18	1,04	b*3	31,11	29,92	-1,19	4,55	
L*Av	58,87	62,50	3,64	a*Av	30,70	32,30	1,60	b*Av	31,11	30,33	-0,78	4,05	
	C												
L*1	59,48	64,04	4,56	a*1	32,14	32,2	0,06	b*1	29,67	28,6	-1,07	4,68	*0,79*
L*2	62,56	64,25	1,69	a*2	30,2	31,63	1,43	b*2	29,89	27,69	-2,2	3,12	
L*3	60,34	64,24	3,9	a*3	31,78	31,93	0,15	b*3	29,66	28,32	-1,34	4,13	
L*Av	60,79	64,18	3,38	a*Av	31,37	31,92	0,55	b*Av	29,74	28,20	-1,54	3,76	
	D												
L*1	53,28	57,37	4,09	a*1	35,98	37,9	1,92	b*1	31,42	32,74	1,32	4,71	*0,51*
L*2	53,32	57,04	3,72	a*2	36,26	38,19	1,93	b*2	31,36	32,82	1,46	4,44	
L*3	53,17	56,49	3,32	a*3	35,51	38,78	3,27	b*3	30,43	33,21	2,78	5,43	
L*Av	53,26	56,97	3,71	a*Av	35,92	38,29	2,37	b*Av	31,07	32,92	1,85	4,78	

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	*Standard deviation*
	E												
L*1	53,13	58,37	5,24	a*1	37,35	37,69	0,34	b*1	32,13	31,23	-0,9	5,33	*0,94*
L*2	52,6	58,94	6,34	a*2	37,58	37,53	-0,05	b*2	31,69	31,84	0,15	6,34	
L*3	53,5	57,51	4,01	a*3	36,49	38,2	1,71	b*3	31,84	30,87	-0,97	4,47	
L*Av	53,08	58,27	5,20	a*Av	37,14	37,81	0,67	b*Av	31,89	31,31	-0,57	5,27	
	F												
L*1	55,38	59,88	4,5	a*1	35,28	35,73	0,45	b*1	29,83	31,99	2,16	5,01	*0,72*
L*2	55,52	59,04	3,52	a*2	36,19	36,42	0,23	b*2	31,15	31,75	0,6	3,58	
L*3	55,24	59,37	4,13	a*3	36,1	36,24	0,14	b*3	31,46	31,87	0,41	4,15	
L*Av	55,38	59,43	4,05	a*Av	35,86	36,13	0,27	b*Av	30,81	31,87	1,06	4,19	
	G												
L*1	52,5	56,75	4,25	a*1	37,09	37,75	0,66	b*1	30,49	30,22	-0,27	4,31	*0,15*
L*2	52,33	56,88	4,55	a*2	37,68	37,79	0,11	b*2	30,81	30,27	-0,54	4,58	
L*3	52,16	56,63	4,47	a*3	36,95	37,63	0,68	b*3	30,16	29,63	-0,53	4,55	
L*Av	52,33	56,75	4,42	a*Av	37,24	37,72	0,48	b*Av	30,49	30,04	-0,45	4,47	
	H												
L*1	52,94	58,31	5,37	a*1	37,23	36,92	-0,31	b*1	30,77	30,72	-0,05	5,38	*0,77*
L*2	53,58	58,88	5,3	a*2	36,45	36,78	0,33	b*2	30,15	31,24	1,09	5,42	
L*3	53,39	56,59	3,2	a*3	35,95	38,1	2,15	b*3	30,23	31,55	1,32	4,07	
L*Av	53,30	57,93	4,62	a*Av	36,54	37,27	0,72	b*Av	30,38	31,17	0,79	4,75	
	I												
L*1	57,4	59,7	2,3	a*1	30,91	33,05	2,14	b*1	29,43	27,97	-1,46	3,46	*1,10*
L*2	57,37	61,68	4,31	a*2	30,43	30,97	0,54	b*2	28,51	27,53	-0,98	4,45	
L*3	56,59	62,03	5,44	a*3	31,66	31,76	0,1	b*3	29,64	28,06	-1,58	5,67	
L*Av	57,12	61,14	4,02	a*Av	31,00	31,93	0,93	b*Av	29,19	27,85	-1,34	4,33	

C.1.7 Colourimetric measurements of Combination3 dyed samples exposed for 536h

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	*Standard deviation*
	Blank sample												
L*1	35,25	37,82	2,57	a*1	51,85	47,18	-4,67	b*1	5,2	6,26	1,06	5,43	*0,10*
L*2	34,49	36,61	2,12	a*2	51,38	46,58	-4,8	b*2	4,58	6,33	1,75	5,53	
L*3	35,4	37,96	2,56	a*3	51,78	47,3	-4,48	b*3	4,74	6,1	1,36	5,34	
L*Av	35,05	37,46	2,42	a*Av	51,67	47,02	-4,65	b*Av	4,84	6,23	1,39	5,42	
	A												
L*1	36,19	39,16	2,97	a*1	53,03	47,68	-5,35	b*1	4,95	5,82	0,87	6,18	*0,34*
L*2	35,45	38,26	2,81	a*2	52,55	47,84	-4,71	b*2	5,8	6,19	0,39	5,50	
L*3	35,93	39,71	3,78	a*3	52,4	47,95	-4,45	b*3	5,3	5,57	0,27	5,84	
L*Av	35,86	39,04	3,19	a*Av	52,66	47,82	-4,84	b*Av	5,35	5,86	0,51	5,81	
	B												
L*1	33	34,23	1,23	a*1	50,53	46,41	-4,12	b*1	6,29	7,47	1,18	4,46	*3,32*
L*2	33,19	34,62	1,43	a*2	48,36	47,3	-1,06	b*2	5,72	7,15	1,43	2,28	
L*3	40,03	34,27	-5,76	a*3	39,82	46,3	6,48	b*3	5,36	6,94	1,58	8,81	
L*Av	35,41	34,37	-1,03	a*Av	46,24	46,67	0,43	b*Av	5,79	7,19	1,40	1,79	
	C												
L*1	33,61	36,12	2,51	a*1	48,98	45,61	-3,37	b*1	5,15	5,59	0,44	4,22	*1,08*
L*2	38,98	37,26	-1,72	a*2	42,62	44,6	1,98	b*2	4,42	5,14	0,72	2,72	
L*3	33,37	36,57	3,2	a*3	48,81	45,23	-3,58	b*3	5,48	5,32	-0,16	4,80	
L*Av	35,32	36,65	1,33	a*Av	46,80	45,15	-1,66	b*Av	5,02	5,35	0,33	2,15	
L*1	33,54	34,66	1,12	a*1	50,93	46,52	-4,41	b*1	5,13	6,5	1,37	4,75	*0,26*
L*2	33,72	35,3	1,58	a*2	50,79	46,54	-4,25	b*2	5,32	6,34	1,02	4,65	
L*3	33,88	34,61	0,73	a*3	50,61	46,79	-3,82	b*3	4,9	6,63	1,73	4,26	
L*Av	33,71	34,86	1,14	a*Av	50,78	46,62	-4,16	b*Av	5,12	6,49	1,37	4,53	

	covered	exposed	ΔL*		covered	exposed	Δa*		covered	exposed	Δb*	ΔE	*Standard deviation*
	E												
	32,19	31,96	-0,23		49,28	44,67	-4,61		6,66	8,11	1,45	4,84	*0,13*
L*1	32,51	33,25	0,74	a*1	49,79	44,81	-4,98	b*1	7,08	7,88	0,8	5,10	
L*2	33,46	33,74	0,28	a*2	49,85	45,2	-4,65	b*2	5,86	7,75	1,89	5,03	
L*3	32,72	32,98	0,26	a*3	49,64	44,89	-4,75	b*3	6,53	7,91	1,38	4,95	
L*Av	F			a*Av				b*Av					
	31,57	32,83	1,26		48,55	45,28	-3,27		8,04	7,76	-0,28	3,52	*0,29*
L*1	32,49	32,43	-0,06	a*1	48,94	45,12	-3,82	b*1	6,65	7,86	1,21	4,01	
L*2	31,73	33,25	1,52	a*2	49,19	45,47	-3,72	b*2	8,11	7,79	-0,32	4,03	
L*3	31,93	32,84	0,91	a*3	48,89	45,29	-3,60	b*3	7,60	7,80	0,20	3,72	
L*Av	G			a*Av				b*Av					
	32,17	32,2	0,03		50,32	46,29	-4,03		8,21	9,25	1,04	4,16	*0,38*
L*1	31,86	31,54	-0,32	a*1	50,71	46,43	-4,28	b*1	8,49	9,87	1,38	4,51	
L*2	32,88	31,92	-0,96	a*2	49,79	46,49	-3,3	b*2	7,34	8,84	1,5	3,75	
L*3	32,30	31,89	-0,42	a*3	50,27	46,40	-3,87	b*3	8,01	9,32	1,31	4,11	
L*Av	H			a*Av				b*Av					
	32,01	32,05	0,04		48,03	44,88	-3,15		7,49	8,29	0,8	3,25	*0,31*
L*1	32,05	32,7	0,65	a*1	48,46	44,88	-3,58	b*1	7,85	8,1	0,25	3,65	
L*2	31,2	32,24	1,04	a*2	48,64	44,98	-3,66	b*2	7,31	7,99	0,68	3,87	
L*3	31,75	32,33	0,58	a*3	48,38	44,91	-3,46	b*3	7,55	8,13	0,58	3,56	
L*Av	I			a*Av				b*Av					
	33,21	34,73	1,52		49,74	45,11	-4,63		6,01	6,28	0,27	4,88	*0,09*
L*1	34,38	35,6	1,22	a*1	49,68	45,14	-4,54	b*1	4,92	5,93	1,01	4,81	
L*2	33,74	34,55	0,81	a*2	50,1	45,27	-4,83	b*2	5,46	6,42	0,96	4,99	
L*3	33,78	34,96	1,18	a*3	49,84	45,17	-4,67	b*3	5,46	6,21	0,75	4,87	
L*Av				a*Av				b*Av					

C. 2 Colourimetric measurements of gradually exposed samples

C.2.1 Colourimetric measurements of madder dyed samples gradually exposed

Inhibitor	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	*ΔE*
Blank sample	non exposed area	60,91	37,67	30,67				
	100h	62,6	35,53	28,91	1,69	-2,14	-1,76	*3,25*
	200h	64,43	37,63	29,54	3,52	-0,04	-1,13	*3,70*
	300h	64,41	36,79	29,33	3,5	-0,88	-1,34	*3,85*
	400h	64,58	36,63	29,89	3,67	-1,04	-0,78	*3,89*
Inhibitor A	non exposed area	62,22	36,95	30,97				
	100h	64,06	36,93	30,72	1,84	-0,02	-0,25	*1,86*
	200h	64,26	35,8	29,58	2,04	-1,15	-1,39	*2,72*
	300h	65,69	34,97	29,75	3,47	-1,98	-1,22	*4,18*
	400h	64,53	35,94	30,12	2,31	-1,01	-0,85	*2,66*
Inhibitor B	non exposed area	62,56	35,11	30,9				
	100h	63,53	36,46	30,12	0,97	1,35	-0,78	*1,84*
	200h	63,39	37,16	30,22	0,83	2,05	-0,68	*2,31*
	300h	64,59	35,9	29,34	2,03	0,79	-1,56	*2,68*
	400h	64,41	36,58	29,89	1,85	1,47	-1,01	*2,57*
Inhibitor C	non exposed area	58,59	40,08	31				
	100h	59,82	41,14	30,87	1,23	1,06	-0,13	*1,63*
	200h	60,39	40,84	30,58	1,8	0,76	-0,42	*2,00*
	300h	61,06	39,43	29,95	2,47	-0,65	-1,05	*2,76*
	400h	62,14	38,97	29,71	3,55	-1,11	-1,29	*3,94*
Inhibitor D	non exposed area	63,23	36,43	30,53				
	100h	64,49	37,09	30,05	1,26	0,66	-0,48	*1,50*
	200h	65,41	36,64	30,1	2,18	0,21	-0,43	*2,23*
	300h	67,73	34,07	28,35	4,5	-2,36	-2,18	*5,53*
	400h	69,06	32,06	27,88	5,83	-4,37	-2,65	*7,75*
Inhibitor E	non exposed aera	53,09	44,48	31,27				
	100h	55,22	45,87	32,41	2,13	1,39	1,14	*2,79*
	200h	55,83	45,4	31,91	2,74	0,92	0,64	*2,96*
	300h	56,35	45,4	31,8	3,26	0,92	0,53	*3,43*
	400h	55,77	44,74	31,85	2,68	0,26	0,58	*2,75*

Inhibitor	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Inhibitor F	non exposed area	57,06	43,01	31,98				
	100h	61,99	40	31,01	4,93	-3,01	-0,97	*5,86*
	200h	62,36	39,39	30,66	5,3	-3,62	-1,32	*6,55*
	300h	63,1	39,14	29,61	6,04	-3,87	-2,37	*7,55*
	400h	61,99	39,63	29,64	4,93	-3,38	-2,34	*6,42*
Inhibitor G	non exposed area	54,96	44,42	31,84				
	100h	59,94	41,42	31	4,98	-3	-0,84	*5,87*
	200h	61,03	41,42	31,14	6,07	-3	-0,7	*6,81*
	300h	62,14	40,24	30,3	7,18	-4,18	-1,54	*8,45*
	400h	63,17	38,43	29,73	8,21	-5,99	-2,11	*10,38*
Inhibitor H	non exposed area	55,71	42,54	31,22				
	100h	53,51	42,16	32,98	-2,2	-0,38	1,76	*2,84*
	200h	55,58	45,08	32,21	-0,13	2,54	0,99	*2,73*
	300h	55,77	45,09	31,77	0,06	2,55	0,55	*2,61*
	400h	55,69	45,54	32,18	-0,02	3	0,96	*3,15*
Inhibitor I	non exposed aera	62,75	35,12	30,62				
	100h	65,44	34,77	30,38	2,69	-0,35	-0,24	*2,72*
	200h	66,2	34,85	30	3,45	-0,27	-0,62	*3,52*
	300h	66,68	35,19	29,57	3,93	0,07	-1,05	*4,07*
	400h	67,3	34,13	29,05	4,55	-0,99	-1,57	*4,91*

C.2.2 Colourimetric measurements of Brazilwood dyed samples gradually exposed

Inhibitors	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Blank sample	non exposed area	36,64	47,87	19,91				
	50h	38,3	43,1	17,8	1,66	-4,77	-2,11	*5,47*
	100h	40,43	40,68	17,9	3,79	-7,19	-2,01	*8,37*
	200h	45,88	35,17	18,09	9,24	-12,7	-1,82	*15,81*
	300h	50,53	30,05	17,89	13,89	-17,82	-2,02	*22,68*
	450h	52,07	28,01	18,07	15,43	-19,86	-1,84	*25,22*
Inhibitor A	non exposed area	37,37	49,17	22,48				
	50h	38,74	47,98	21,67	1,37	-1,19	-0,81	*1,99*
	100h	41,31	41,86	19,01	3,94	-7,31	-3,47	*9,00*
	200h	46,55	35,73	18,18	9,18	-13,44	-4,3	*16,83*
	300h	50,27	31,6	18,13	12,9	-17,57	-4,35	*22,23*
	450h	53,28	28,07	18,47	15,91	-21,1	-4,01	*26,73*
Inhibitor B	non exposed area	36,98	46,08	20,35				
	50h	36,69	45,06	19,83	-0,29	-1,02	-0,52	*1,18*
	100h	39,47	39,94	17,7	2,49	-6,14	-2,65	*7,14*
	200h	44,67	34,91	17,53	7,69	-11,17	-2,82	*13,85*
	300h	47,6	32,01	17,72	10,62	-14,07	-2,63	*17,82*
	450h	51,14	28,14	17,95	14,16	-17,94	-2,4	*22,98*
Inhibitor C	non exposed area	37,56	44,7	19,45				
	50h	38,41	42,35	18,17	0,85	-2,35	-1,28	*2,81*
	100h	39,8	40,63	17,35	2,24	-4,07	-2,1	*5,10*
	200h	45,06	34,12	16,76	7,5	-10,58	-2,69	*13,24*
	300h	49,1	30,39	16,46	11,54	-14,31	-2,99	*18,62*
	450h	49,91	29,01	17,27	12,35	-15,69	-2,18	*20,09*
Inhibitor D	non exposed area	35,29	47,92	19,58				
	50h	35,68	45,05	18,89	0,39	-2,87	-0,69	*2,98*
	100h	39,67	39,76	17,81	4,38	-8,16	-1,77	*9,43*
	200h	45,1	34,46	17,93	9,81	-13,46	-1,65	*16,74*
	300h	48,76	31,14	18,25	13,47	-16,78	-1,33	*21,56*
	450h	52,55	27,34	18,09	17,26	-20,58	-1,49	*26,90*
Inhibitor E	non exposed area	34,23	44,59	18,26				
	50h	38,49	40,45	17,22	4,26	-4,14	-1,04	*6,03*
	100h	40,29	39,99	17,42	6,06	-4,6	-0,84	*7,65*
	200h	42,48	35,8	17,57	8,25	-8,79	-0,69	*12,07*
	300h	46,75	32,52	17,81	12,52	-12,07	-0,45	*17,40*
	450h	47,86	30,74	18,36	13,63	-13,85	0,1	*19,43*
Inhibitor F	non exposed area	35,65	46,23	19,43				
	50h	40,02	40,02	17,48	4,37	-6,21	-1,95	*7,84*
	100h	41,17	39,74	17,99	5,52	-6,49	-1,44	*8,64*
	200h	41,37	30,24	15,71	5,72	-15,99	-3,72	*17,38*
	300h	48,42	31,97	18,04	12,77	-14,26	-1,39	*19,19*
	450h	51,08	28,85	17,96	15,43	-17,38	-1,47	*23,29*

Appendix C: Light fading tests

Inhibitors	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	*ΔE*
Inhibitor G	non exposed area	33,64	46,27	18,46				
	50h	37,99	40,13	17,41	4,35	-6,14	-1,05	*7,60*
	100h	39,58	39,36	17,39	5,94	-6,91	-1,07	*9,17*
	200h	44,02	34,23	17,93	10,38	-12,04	-0,53	*15,91*
	300h	47,84	30	17,72	14,2	-16,27	-0,74	*21,61*
	450h	52,07	26,38	18,16	18,43	-19,89	-0,3	*27,12*
Inhibitor H	non exposed area	35,73	45,1	18,73				
	50h	38,26	40,08	17	2,53	-5,02	-1,73	*5,88*
	100h	39,51	39,34	17,06	3,78	-5,76	-1,67	*7,09*
	200h	42,78	35,47	17,56	7,05	-9,63	-1,17	*11,99*
	300h	45,41	32,68	17,48	9,68	-12,42	-1,25	*15,80*
	450h	48,82	29,46	17,65	13,09	-15,64	-1,08	*20,42*
Inhibitor I	non exposed area	37,07	48,01	18,87				
	50h	40,61	39,77	16,71	3,54	-8,24	-2,16	*9,22*
	100h	41,84	38,71	16,91	4,77	-9,3	-1,96	*10,63*
	200h	45,31	34,57	17,18	8,24	-13,44	-1,69	*15,86*
	300h	47,97	30,78	16,68	10,9	-17,23	-2,19	*20,51*
	450h	51,24	27,58	17,06	14,17	-20,43	-1,81	*24,93*

C.2.3 Colourimetric measurements of Safflower dyed samples gradually exposed

Inhibitors	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	*ΔE*
Blank sample	non exposed area	80,15	30,28	17,83				
	50h	82,24	25,71	20,61	2,09	-4,57	2,78	*5,74*
	100h	91,01	5,22	17,52	10,86	-25,06	-0,31	*27,31*
	200h	92,97	1,92	12,79	12,82	-28,36	-5,04	*31,53*
	300h	93,73	0,8	11,24	13,58	-29,48	-6,59	*33,12*
	450h	93,86	0,33	10,5	13,71	-29,95	-7,33	*33,74*
Inhibitor A	non exposed area	81,33	29,05	19,54				
	50h	83,79	22,09	23,6	2,46	-6,96	4,06	*8,42*
	100h	91,85	3,69	16,69	10,52	-25,36	-2,85	*27,60*
	200h	93,29	1,49	12,85	11,96	-27,56	-6,69	*30,78*
	300h	93,78	0,73	11,42	12,45	-28,32	-8,12	*31,98*
	450h	93,75	-0,09	10,91	12,42	-29,14	-8,63	*32,83*
Inhibitor B	non exposed area	80,16	30,73	20,2				
	50h	88,19	9,84	21,94	8,03	-20,89	1,74	*22,45*
	100h	90,39	5,42	19,23	10,23	-25,31	-0,97	*27,32*
	200h	92,01	2,58	15,4	11,85	-28,15	-4,8	*30,92*
	300h	92,81	1,45	13,4	12,65	-29,28	-6,8	*32,61*
	450h	92,89	0,92	12,48	12,73	-29,81	-7,72	*33,32*
Inhibitor C	non exposed area	80,9	29,8	19,45				
	50h	88,42	8,77	24,18	7,52	-21,03	4,73	*22,83*
	100h	90,31	5,16	20,8	9,41	-24,64	1,35	*26,41*
	200h	91,42	3,35	17,63	10,52	-26,45	-1,82	*28,52*
	300h	92,85	1,49	15	11,95	-28,31	-4,45	*31,05*
	450h	93,28	0,71	13,44	12,38	-29,09	-6,01	*32,18*
Inhibitor D	non exposed area	79,8	30,39	21,01				
	50h	85,02	17,45	24	5,22	-12,94	2,99	*14,27*
	100h	90,93	4,75	18,32	11,13	-25,64	-2,69	*28,08*
	200h	93,01	1,54	13,35	13,21	-28,85	-7,66	*32,64*
	300h	93,62	0,55	11,97	13,82	-29,84	-9,04	*34,10*
	450h	93,82	0,11	11,42	14,02	-30,28	-9,59	*34,72*
Inhibitor E	non exposed area	80,42	30,42	20,42				
	50h	84,69	19,11	23,71	4,27	-11,31	3,29	*12,53*
	100h	91,24	4,35	18	10,82	-26,07	-2,42	*28,33*
	200h	91,98	1,9	14,38	11,56	-28,52	-6,04	*31,36*
	300h	93,56	0,67	11,39	13,14	-29,75	-9,03	*33,75*
	450h	92,91	0,42	11,27	12,49	-30	-9,15	*33,76*
Inhibitor F	non exposed area	79,73	30,4	22,5				
	50h	86,75	10,56	22,71	7,02	-19,84	0,21	*21,05*
	100h	89,77	4,65	19,6	10,04	-25,75	-2,9	*27,79*
	200h	91,86	2,1	14,72	12,13	-28,3	-7,78	*31,76*
	300h	92,56	1,13	12,9	12,83	-29,27	-9,6	*33,37*
	450h	92,72	0,7	12,33	12,99	-29,7	-10,17	*33,97*

Appendix C: Light fading tests

Inhibitors	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Inhibitor G	non exposed area	80,17	29,93	21,6				
	50h	87,06	11,75	21,47	6,89	-18,18	-0,13	*19,44*
	100h	90,91	3,47	16,71	10,74	-26,46	-4,89	*28,97*
	200h	91,86	1,82	14,04	11,69	-28,11	-7,56	*31,37*
	300h	92,59	0,82	12,39	12,42	-29,11	-9,21	*32,96*
	450h	92,95	0,28	11,44	12,78	-29,65	-10,16	*33,85*
Inhibitor H	non exposed area	78,17	32,94	21,41				
	50h	87,84	8,44	25,07	9,67	-24,5	3,66	*26,59*
	100h	89,61	4,97	21,17	11,44	-27,97	-0,24	*30,22*
	200h	91,12	2,64	17,04	12,95	-30,3	-4,37	*33,24*
	300h	91,86	1,48	14,93	13,69	-31,46	-6,48	*34,92*
	450h	91,89	1,27	14,58	13,72	-31,67	-6,83	*35,18*
Inhibitor I	non exposed area	78,5	33,09	21,72				
	50h	88,11	9,42	23,7	9,61	-23,67	1,98	*25,62*
	100h	90,29	5,29	20,23	11,79	-27,8	-1,49	*30,23*
	200h	91,96	2,58	15,99	13,46	-30,51	-5,73	*33,84*
	300h	92,79	1,8	14,19	14,29	-31,29	-7,53	*35,21*
	450h	92,76	1,41	13,37	14,26	-31,68	-8,35	*35,73*

C.2.4 Colourimetric measurements of Cochineal dyed samples gradually exposed

Inhibitor	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	*ΔE*
Blank sample	non exposed area	30,98	44,84	10,74				
	100h	32,67	44,98	11,39	1,69	0,14	0,65	*1,82*
	200h	32,44	44,33	11,05	1,46	-0,51	0,31	*1,58*
	300h	34,94	44,27	10,37	3,96	-0,57	-0,37	*4,02*
	400h	34,86	44,58	10,75	3,88	-0,26	0,01	*3,89*
Inhibitor A	non exposed area	29,82	48,44	13,02				
	100h	31,97	46,65	12,22	2,15	-1,79	-0,8	*2,91*
	200h	31,61	45,1	11,28	1,79	-3,34	-1,74	*4,17*
	300h	34,57	46,26	11,53	4,75	-2,18	-1,49	*5,43*
	400h	34,78	44,5	10,67	4,96	-3,94	-2,35	*6,76*
Inhibitor B	non exposed area	28,62	41,44	9,3				
	100h	30,77	42,47	10,07	2,15	1,03	0,77	*2,51*
	200h	31,49	42,31	9,64	2,87	0,87	0,34	*3,02*
	300h	31,94	42,39	9,44	3,32	0,95	0,14	*3,46*
	400h	33,31	42,5	9,21	4,69	1,06	-0,09	*4,81*
Inhibitor C	non exposed area	33,25	39,05	6,22				
	100h	35,17	37,48	6,47	1,92	-1,57	0,25	*2,49*
	200h	34,78	37,63	6,59	1,53	-1,42	0,37	*2,12*
	300h	36,21	38,85	6,91	2,96	-0,2	0,69	*3,05*
	400h	36,17	37,58	6,33	2,92	-1,47	0,11	*3,27*
Inhibitor D	non exposed area	29,36	43,69	9,42				
	100h	29,83	42,6	11,17	0,47	-1,09	1,75	*2,11*
	200h	31,85	42,48	10,27	2,49	-1,21	0,85	*2,90*
	300h	31,85	42,2	10,35	2,49	-1,49	0,93	*3,05*
	400h	32,22	42,48	10,14	2,86	-1,21	0,72	*3,19*
Inhibitor E	non exposed area	30,63	41,57	9,9				
	100h	31,74	41,74	9,99	1,11	0,17	0,09	*1,13*
	200h	31,82	41,31	9,89	1,19	-0,26	-0,01	*1,22*
	300h	33,09	42,05	10,14	2,46	0,48	0,24	*2,52*
	400h	33,85	42,61	10,29	3,22	1,04	0,39	*3,41*

Appendix C: Light fading tests

Inhibitor	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Inhibitor F	non exposed area	30,99	41,82	10,12				
	100h	30,5	42,51	10,89	-0,49	0,69	0,77	*1,14*
	200h	31,1	42,32	10,91	0,11	0,5	0,79	*0,94*
	300h	31,38	42,18	10,67	0,39	0,36	0,55	*0,76*
	400h	32,2	42,31	10,41	1,21	0,49	0,29	*1,34*
Inhibitor G	non exposed area	30,06	42,61	9,85				
	100h	32,25	39,88	9,82	2,19	-2,73	-0,03	*3,50*
	200h	32,19	41,78	9,47	2,13	-0,83	-0,38	*2,32*
	300h	33,17	42,13	9,54	3,11	-0,48	-0,31	*3,16*
	400h	35,27	42,63	9,94	5,21	0,02	0,09	*5,21*
Inhibitor H	non exposed area	30,94	40,47	8,96				
	100h	31,27	39,64	9,11	0,33	-0,83	0,15	*0,91*
	200h	31,92	40,96	9,48	0,98	0,49	0,52	*1,21*
	300h	33,01	40,27	9,04	2,07	-0,2	0,08	*2,08*
	400h	33,54	41,06	9,17	2,6	0,59	0,21	*2,67*
Inhibitor I	non exposed area	32,12	39,87	7,5				
	100h	33,08	40,39	8,5	0,96	0,52	1	*1,48*
	200h	33	39,63	7,9	0,88	-0,24	0,4	*1,00*
	300h	34,46	40	7,74	2,34	0,13	0,24	*2,36*
	400h	35,33	37,82	6,87	3,21	-2,05	-0,63	*3,86*

C.2.5 Colourimetric measurements of Combination 1 dyed samples gradually exposed

Inhibitors	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	*ΔE*
Blank sample	non exposed area	56,77	37,76	31,27				
	100h	59,77	35,9	31,03	3	-1,86	-0,24	*3,54*
	200h	61,25	35,35	30,52	4,48	-2,41	-0,75	*5,14*
	300h	61,09	35,99	30,78	4,32	-1,77	-0,49	*4,69*
	400h	62,8	33,99	29,76	6,03	-3,77	-1,51	*7,27*
Inhibitor A	non exposed area	57,14	38,74	32,69				
	100h	60,8	37,52	32,49	3,66	-1,22	-0,2	*3,86*
	200h	63,28	35,93	32,07	6,14	-2,81	-0,62	*6,78*
	300h	62,12	37,16	32,06	4,98	-1,58	-0,63	*5,26*
	400h	62,39	37,12	31,42	5,25	-1,62	-1,27	*5,64*
Inhibitor B	non exposed area	55,8	38,42	31,96				
	100h	62,26	36,04	31,69	6,46	-2,38	-0,27	*6,89*
	200h	60,69	37,41	31,79	4,89	-1,01	-0,17	*5,00*
	300h	60,14	37,51	31,46	4,34	-0,91	-0,5	*4,46*
	400h	62,85	35,86	30,82	7,05	-2,56	-1,14	*7,59*
Inhibitor C	non exposed area	59,32	33,09	29,46				
	100h	60,24	32,48	27,98	0,92	-0,61	-1,48	*1,85*
	200h	61,57	32,6	28,58	2,25	-0,49	-0,88	*2,47*
	300h	62,34	32,42	28,44	3,02	-0,67	-1,02	*3,26*
	400h	64,06	30,91	27,45	4,74	-2,18	-2,01	*5,59*
Inhibitor D	non exposed area	55,14	36,74	31,58				
	100h	58,16	36,77	30,9	3,02	0,03	-0,68	*3,10*
	200h	58,61	36,9	31,55	3,47	0,16	-0,03	*3,47*
	300h	58,64	36,29	31,78	3,5	-0,45	0,2	*3,53*
	400h	60,81	35,82	31,46	5,67	-0,92	-0,12	*5,75*
Inhibitor E	non exposed area	55,48	37,69	33				
	100h	58,43	38,18	34,42	2,95	0,49	1,42	*3,31*
	200h	58,25	38,06	33,93	2,77	0,37	0,93	*2,95*
	300h	58,98	37,89	33,6	3,5	0,2	0,6	*3,56*
	400h	60,66	37,06	31,98	5,18	-0,63	-1,02	*5,32*

Appendix C: Light fading tests

Inhibitors	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Inhibitor F	non exposed area	54,46	38,73	32				
	100h	58,01	37,1	31,51	3,55	-1,63	-0,49	*3,94*
	200h	57,11	38,3	32,64	2,65	-0,43	0,64	*2,76*
	300h	57,97	38,38	32,7	3,51	-0,35	0,7	*3,60*
	400h	60,16	37,22	32,06	5,7	-1,51	0,06	*5,90*
Inhibitor G	non exposed area	56,33	36,57	30,66				
	100h	63,08	33,04	30,79	6,75	-3,53	0,13	*7,62*
	200h	63,26	33,63	29,97	6,93	-2,94	-0,69	*7,56*
	300h	63,87	32,6	29,63	7,54	-3,97	-1,03	*8,58*
	400h	64,94	32,35	29,19	8,61	-4,22	-1,47	*9,70*
Inhibitor H	non exposed area	56,98	37,57	31,31				
	100h	57,88	37,84	32,63	0,9	0,27	1,32	*1,62*
	200h	58,47	37,63	32,21	1,49	0,06	0,9	*1,74*
	300h	60,28	36,97	32,91	3,3	-0,6	1,6	*3,72*
	400h	60,87	36,89	32,01	3,89	-0,68	0,7	*4,01*
Inhibitor I	non exposed area	55,6	37,68	30,2				
	100h	58,97	36,67	30,44	3,37	-1,01	0,24	*3,53*
	200h	60,64	35,76	29,69	5,04	-1,92	-0,51	*5,42*
	300h	61,36	35,46	29,1	5,76	-2,22	-1,1	*6,27*
	400h	62,16	34,84	28,74	6,56	-2,84	-1,46	*7,30*

C.2.6 Colourimetric measurements of Combination 2 dyed samples gradually exposed

Inhibitors	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	*ΔE*
Blank sample	non exposed area	56,77	37,76	31,27				
	100h	58,77	35,9	31,03	2	-1,86	-0,24	*2,74*
	200h	61,3	35,5	30,32	4,53	-2,26	-0,95	*5,15*
	300h	61,09	35,99	30,58	4,32	-1,77	-0,69	*4,72*
	400h	63,8	32,99	29,76	7,03	-4,77	-1,51	*8,63*
Inhibitor A	non exposed area	57,14	38,74	32,69				
	100h	60,8	35,52	32,59	3,66	-3,22	-0,1	*4,88*
	200h	62,28	35,93	32,07	5,14	-2,81	-0,62	*5,89*
	300h	62,12	37,16	31,06	4,98	-1,58	-1,63	*5,47*
	400h	62,39	37,02	31,42	5,25	-1,72	-1,27	*5,67*
Inhibitor B	non exposed area	54,8	38,42	31,96				
	100h	60,26	36,04	31,69	5,46	-2,38	-0,27	*5,96*
	200h	60,69	37,41	31,79	5,89	-1,01	-0,17	*5,98*
	300h	61,14	37,51	30,46	6,34	-0,91	-1,5	*6,58*
	400h	62,85	37,86	30,82	8,05	-0,56	-1,14	*8,15*
Inhibitor C	non exposed area	59,22	33,09	30,46				
	100h	60,24	32,5	27,98	1,02	-0,59	-2,48	*2,75*
	200h	61,37	32,6	28,6	2,15	-0,49	-1,86	*2,88*
	300h	63,34	32,22	28,44	4,12	-0,87	-2,02	*4,67*
	400h	64,06	30,91	28,45	4,84	-2,18	-2,01	*5,68*
Inhibitor D	non exposed area	54,14	35,74	30,58				
	100h	58,16	36,77	30,9	4,02	1,03	0,32	*4,16*
	200h	58,5	36,9	31,55	4,36	1,16	0,97	*4,61*
	300h	58,62	36,32	31,8	4,48	0,58	1,22	*4,68*
	400h	60,75	35,8	31,46	6,61	0,06	0,88	*6,67*
Inhibitor E	non exposed area	55,48	36,69	33,45				
	100h	57,43	38,18	34,42	1,95	1,49	0,97	*2,64*
	200h	58,25	38,15	33,98	2,77	1,46	0,53	*3,18*
	300h	58,98	37,89	33,64	3,5	1,2	0,19	*3,70*
	400h	60,54	38,06	33,98	5,06	1,37	0,53	*5,27*

Appendix C: Light fading tests

Inhibitors	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Inhibitor F	non exposed area	55,15	37,73	32,76				
	100h	56,01	37,1	32,51	0,86	-0,63	-0,25	*1,09*
	200h	57,11	38,3	32,79	1,96	0,57	0,03	*2,04*
	300h	58,8	38,28	32,7	3,65	0,55	-0,06	*3,69*
	400h	60,16	38,22	32,06	5,01	0,49	-0,7	*5,08*
Inhibitor G	non exposed area	58,33	35,57	30,66				
	100h	63,08	33,04	29,79	4,75	-2,53	-0,87	*5,45*
	200h	63,3	32,63	29,97	4,97	-2,94	-0,69	*5,82*
	300h	63,87	32,6	29,45	5,54	-2,97	-1,21	*6,40*
	400h	64,78	32,35	28,19	6,45	-3,22	-2,47	*7,62*
Inhibitor H	non exposed area	54,98	36,57	31,31				
	100h	57,78	37,84	31,63	2,8	1,27	0,32	*3,09*
	200h	58,47	37,63	32,21	3,49	1,06	0,9	*3,76*
	300h	60,23	38,97	32,75	5,25	2,4	1,44	*5,95*
	400h	60,17	38,89	33,01	5,19	2,32	1,7	*5,93*
Inhibitor I	non exposed area	57,6	37,68	30,2				
	100h	58,97	37,67	30,07	1,37	-0,01	-0,13	*1,38*
	200h	60,45	36,76	29,69	2,85	-0,92	-0,51	*3,04*
	300h	61,16	35,34	28,1	3,56	-2,34	-2,1	*4,75*
	400h	62,26	34,84	28,74	4,66	-2,84	-1,46	*5,65*

C.2.7 Colourimetric measurements of Combination 3 dyed samples gradually exposed

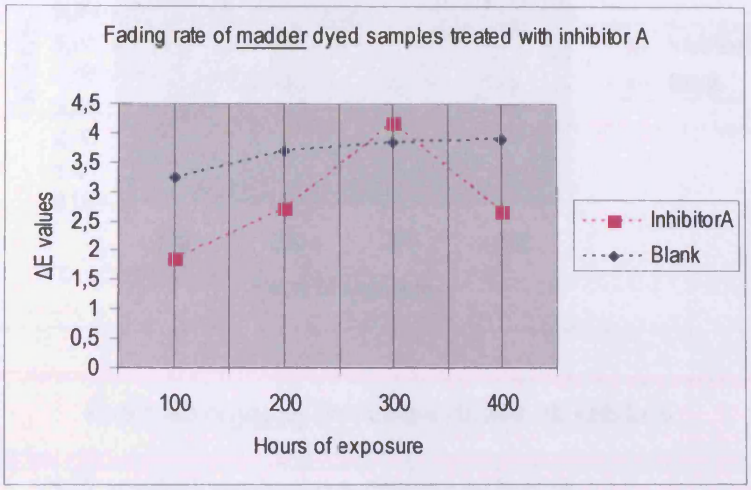
Inhibitor	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	*ΔE*
Blank sample	non exposed area	33,23	50,55	7,09				
	100h	32,89	47,85	7,97	-0,34	-2,7	0,88	*2,86*
	200h	32,96	47,36	8,18	-0,27	-3,19	1,09	*3,38*
	300h	33,07	46,78	8,15	-0,16	-3,77	1,06	*3,92*
	400h	34,75	45,57	7,81	1,52	-4,98	0,72	*5,26*
Inhibitor A	non exposed area	35,6	51,01	6,15				
	100h	35,74	49,35	5,09	0,14	-1,66	-1,06	*1,97*
	200h	35,8	47,92	6,66	0,2	-3,09	0,51	*3,14*
	300h	36,42	47,44	6,69	0,82	-3,57	0,54	*3,70*
	400h	37,2	46,72	6,62	1,6	-4,29	0,47	*4,60*
Inhibitor B	non exposed area	34,79	49,14	4,91				
	100h	34,38	47,75	7,54	-0,41	-1,39	2,63	*3,00*
	200h	35,34	47,32	7,59	0,55	-1,82	2,68	*3,29*
	300h	35,38	46,16	7,45	0,59	-2,98	2,54	*3,96*
	400h	34,65	45,48	7,53	-0,14	-3,66	2,62	*4,50*
Inhibitor C	non exposed area	37,02	43,21	2,43				
	100h	37,47	42,29	3,19	0,45	-0,92	0,76	*1,28*
	200h	36,9	42,29	3,61	-0,12	-0,92	1,18	*1,50*
	300h	37,82	41,62	3,52	0,8	-1,59	1,09	*2,09*
	400h	38,78	40,48	3,62	1,76	-2,73	1,19	*3,46*
Inhibitor D	non exposed area	30,46	48,58	9,29				
	100h	30,45	45,15	9,81	-0,01	-3,43	0,52	*3,47*
	200h	29,26	45,8	10,51	-1,2	-2,78	1,22	*3,26*
	300h	29,82	45,44	10,12	-0,64	-3,14	0,83	*3,31*
	400h	30,5	44,73	9,82	0,04	-3,85	0,53	*3,89*
Inhibitor E	non exposed area	31,5	47,29	8,89				
	100h	31,46	46,96	8,99	-0,04	-0,33	0,1	*0,35*
	200h	31,46	45,28	8,94	-0,04	-2,01	0,05	*2,01*
	300h	31,6	45,33	8,5	0,1	-1,96	-0,39	*2,00*
	400h	33	45,36	8,66	1,5	-1,93	-0,23	*2,46*

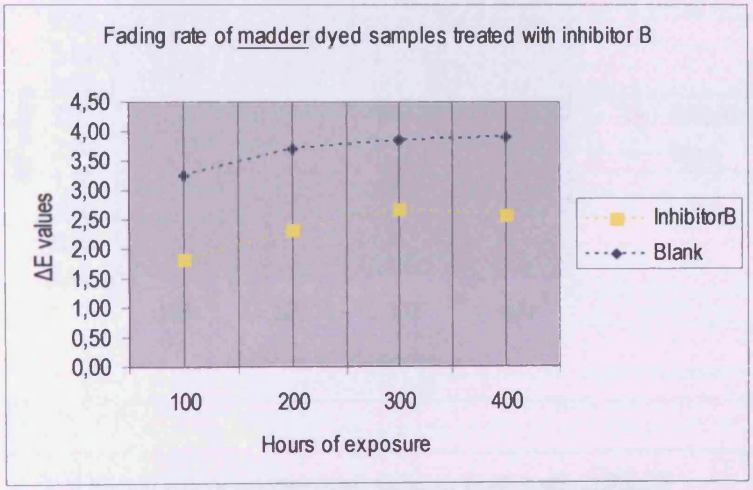
Inhibitor	Hours of exposure	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Inhibitor F	non exposed area	33,55	49,65	6,4				
	100h	32,31	47,41	8,39	-1,24	-2,24	1,99	*3,24*
	200h	34,2	47,82	6,82	0,65	-1,83	0,42	*1,99*
	300h	33,99	46,3	6,98	0,44	-3,35	0,58	*3,43*
	400h	34,97	45,96	6,95	1,42	-3,69	0,55	*3,99*
Inhibitor G	non exposed area	33,45	50,38	4,07				
	100h	31,28	49,03	9,11	-2,17	-1,35	5,04	*5,65*
	200h	29,88	47,67	9,57	-3,57	-2,71	5,5	*7,09*
	300h	31,53	46,39	9,18	-1,92	-3,99	5,11	*6,76*
	400h	31,67	46,39	9,49	-1,78	-3,99	5,42	*6,96*
Inhibitor H	non exposed area	33,74	48,28	6,87				
	100h	32,75	45,84	6,83	-0,99	-2,44	-0,04	*2,63*
	200h	31,9	44,84	7,47	-1,84	-3,44	0,6	*3,95*
	300h	33,38	44,43	6,78	-0,36	-3,85	-0,09	*3,87*
	400h	33,72	44,19	7,22	-0,02	-4,09	0,35	*4,10*
Inhibitor I	non exposed area	35,9	50,18	1,96				
	100h	31,92	46,14	6,32	-3,98	-4,04	4,36	*7,15*
	200h	30,99	46,66	8,64	-4,91	-3,52	6,68	*9,01*
	300h	32,9	46,6	5,75	-3	-3,58	3,79	*6,02*
	400h	33,71	44,65	5,95	-2,19	-5,53	3,99	*7,16*

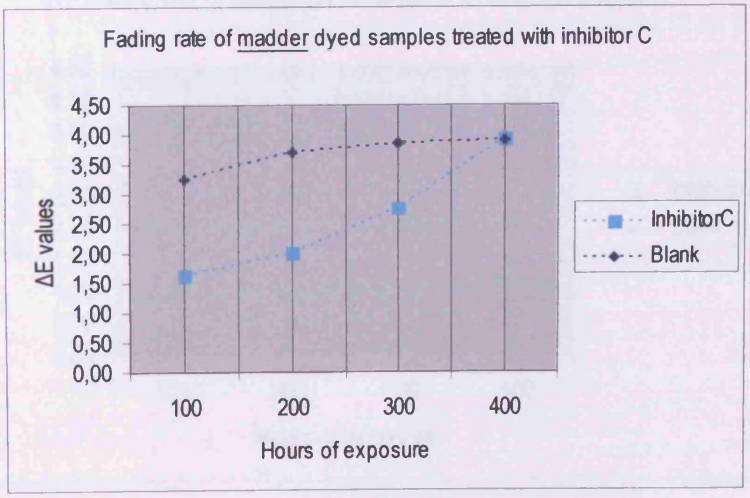
C.3 Fading rates of gradually exposed samples

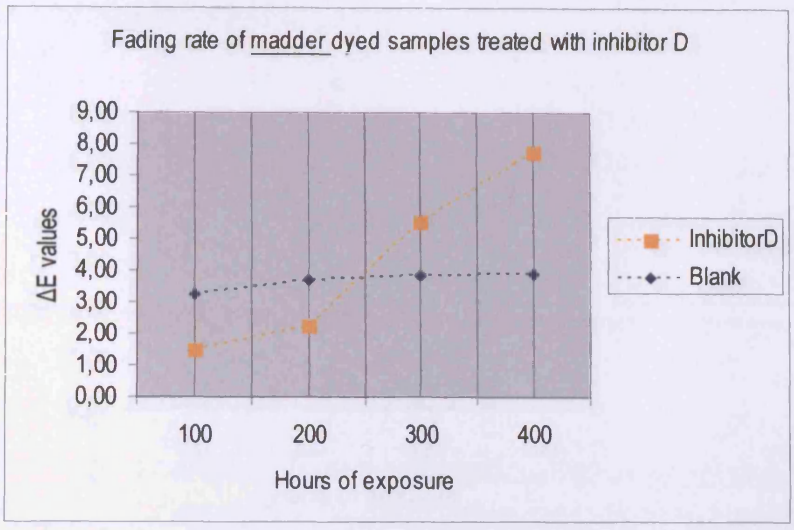
Dotted lines are only for visual effect

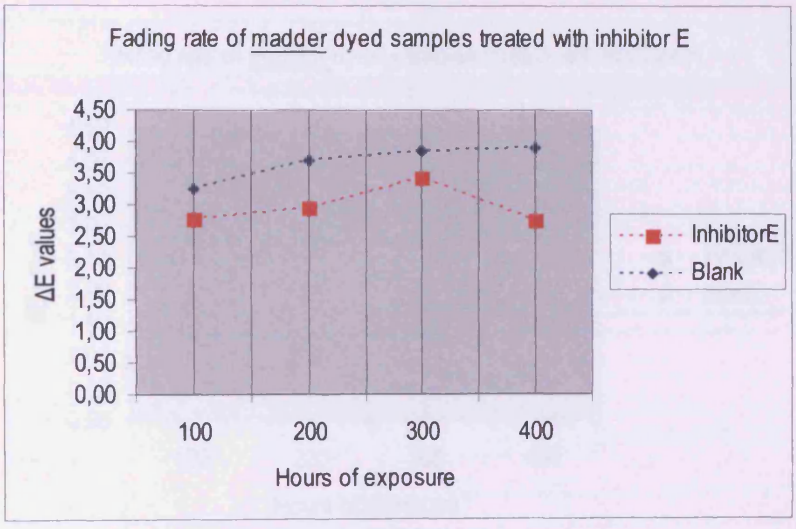
C.3.1 Fading rates of Madder dyed samples

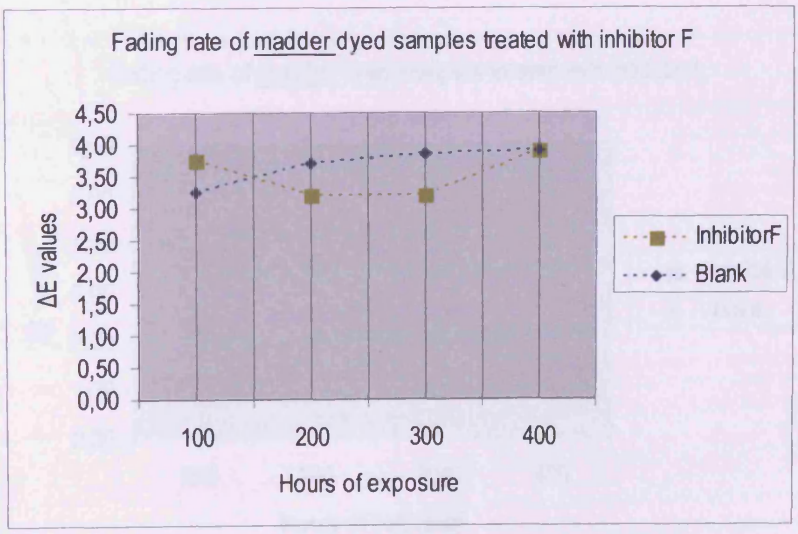


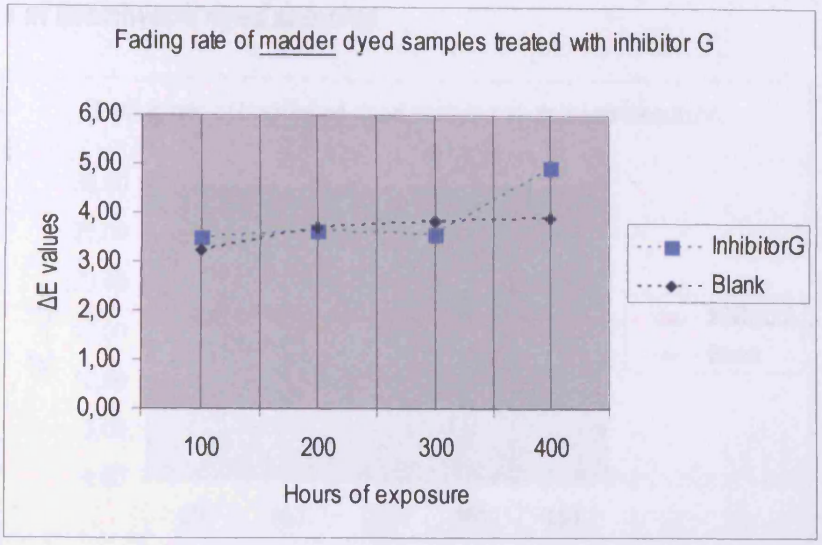


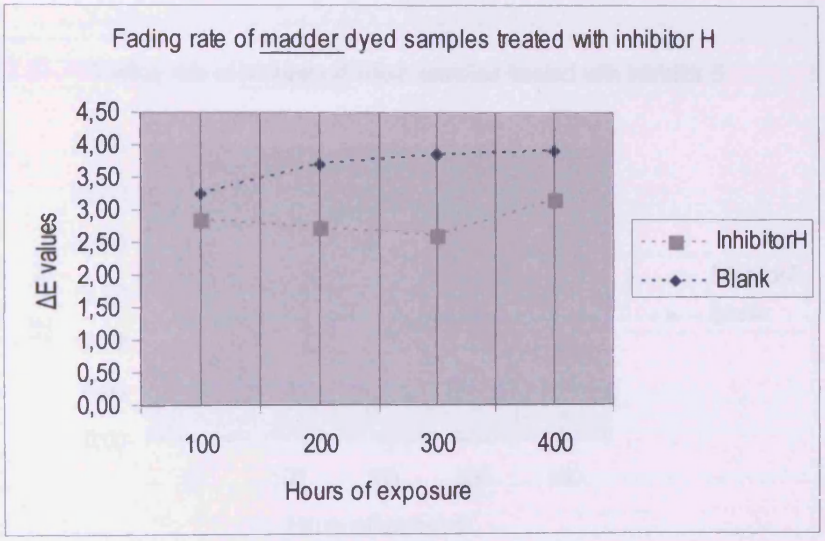


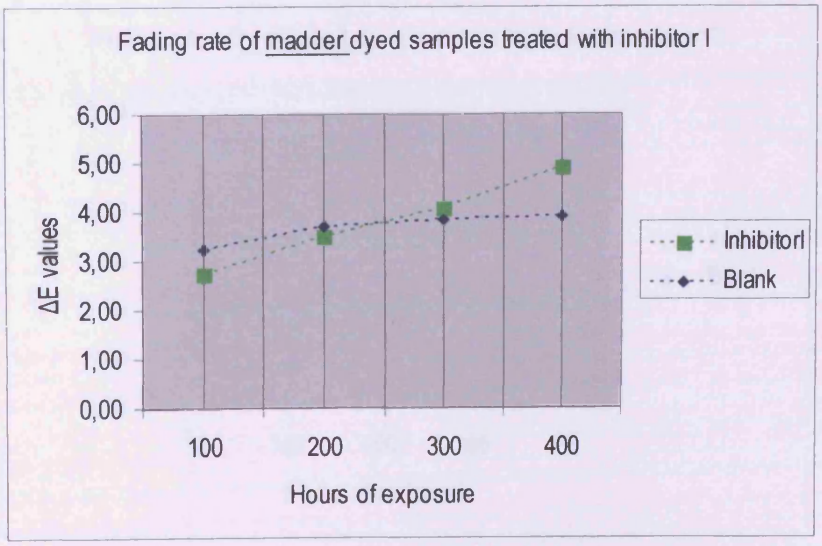

Fading rate of madder dyed samples treated with inhibitor D
ΔE values
9,00
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
100
200
300
400
Hours of exposure
InhibitorD
Blank


Fading rate of madder dyed samples treated with inhibitor E
ΔE values
4,50
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
100
200
300
400
Hours of exposure
InhibitorE
Blank

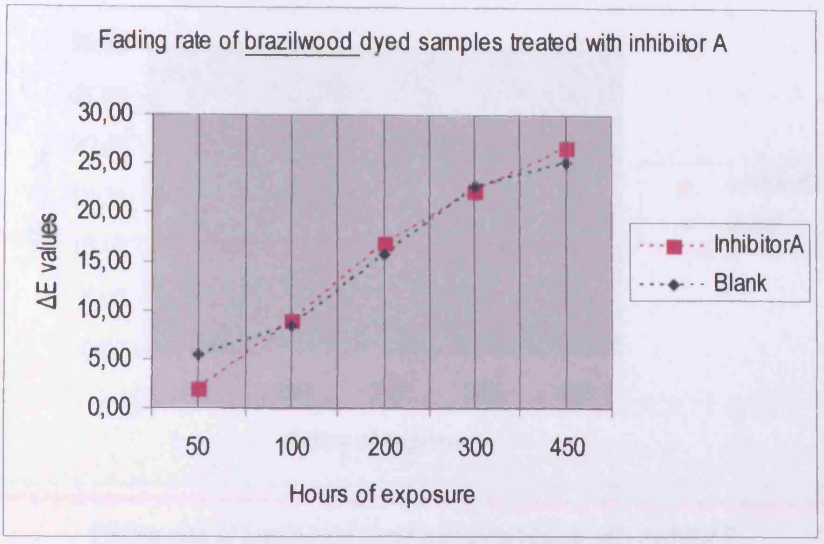

Fading rate of madder dyed samples treated with inhibitor F
ΔE values
4,50
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
100
200
300
400
Hours of exposure
InhibitorF
Blank

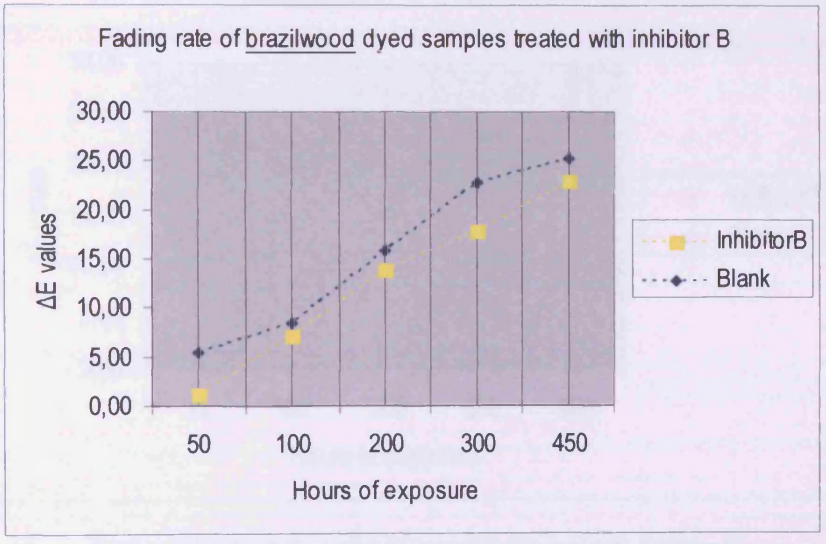

Fading rate of madder dyed samples treated with inhibitor G
6,00
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorG
Blank

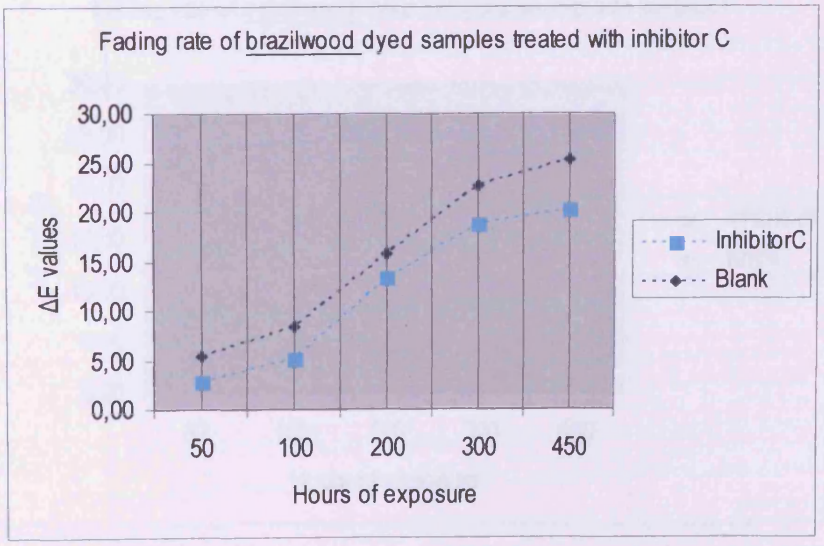

Fading rate of madder dyed samples treated with inhibitor H
4,50
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorH
Blank

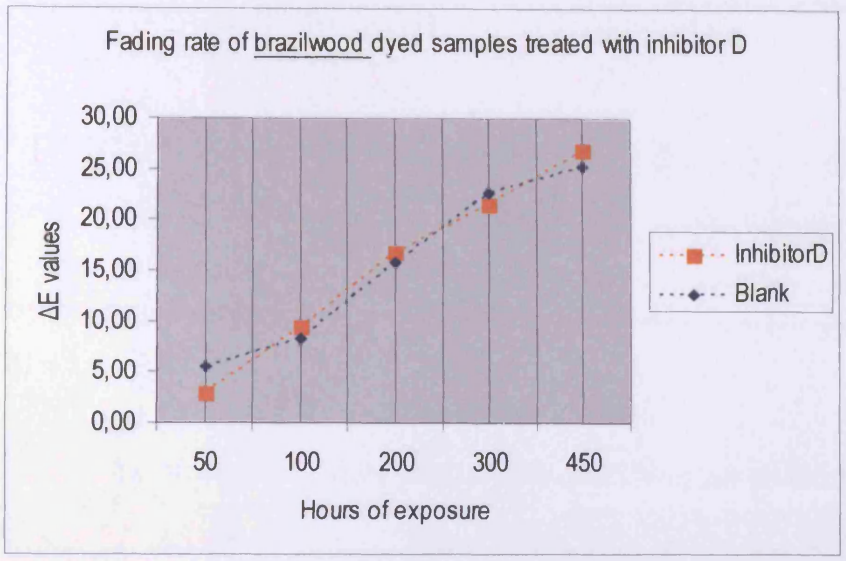

Fading rate of madder dyed samples treated with inhibitor I
6,00
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorI
Blank

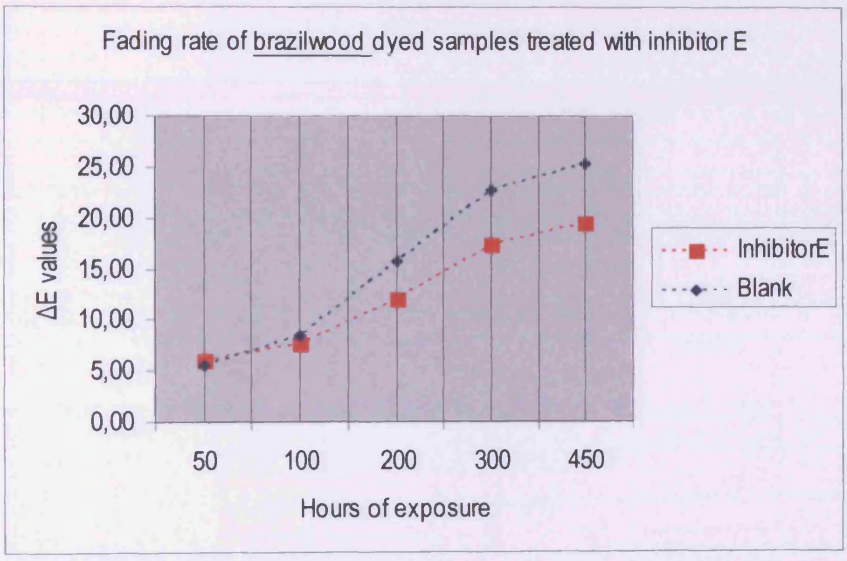
C.3.2 Fading rates of Brazilwood dyed samples

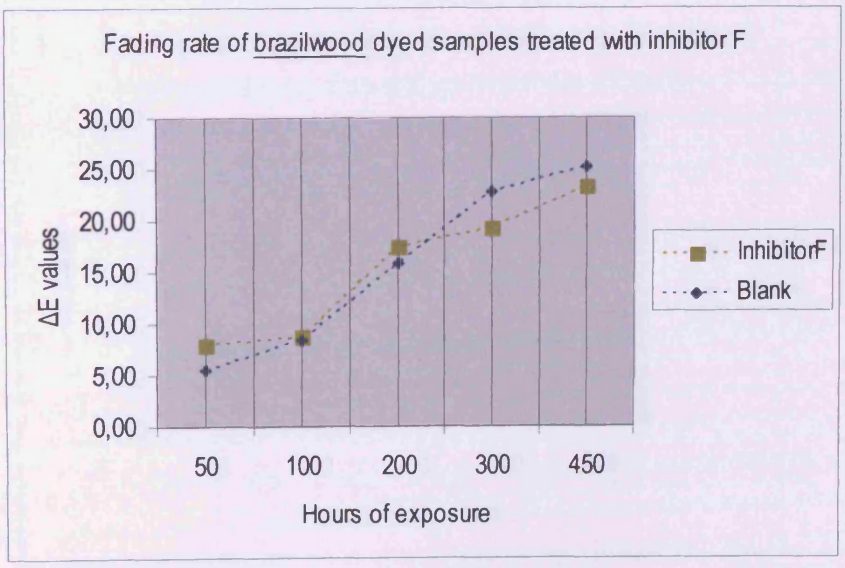


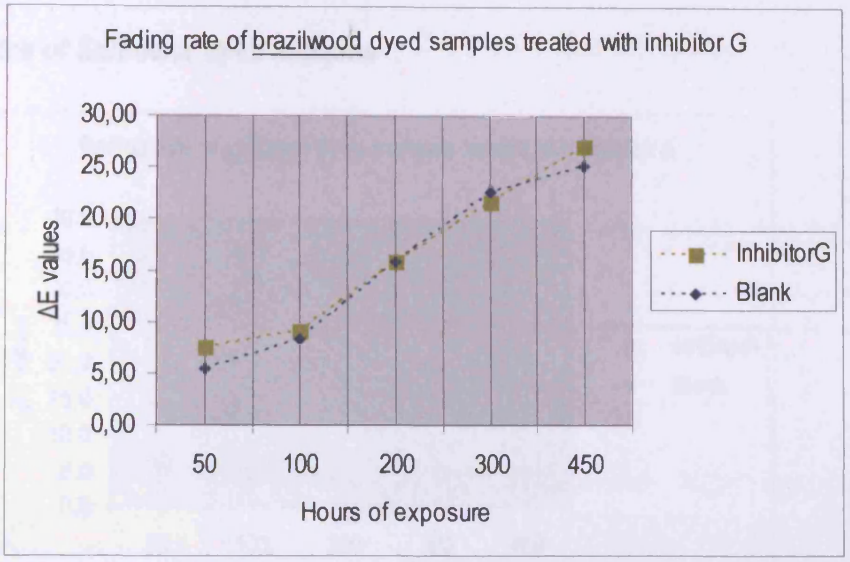


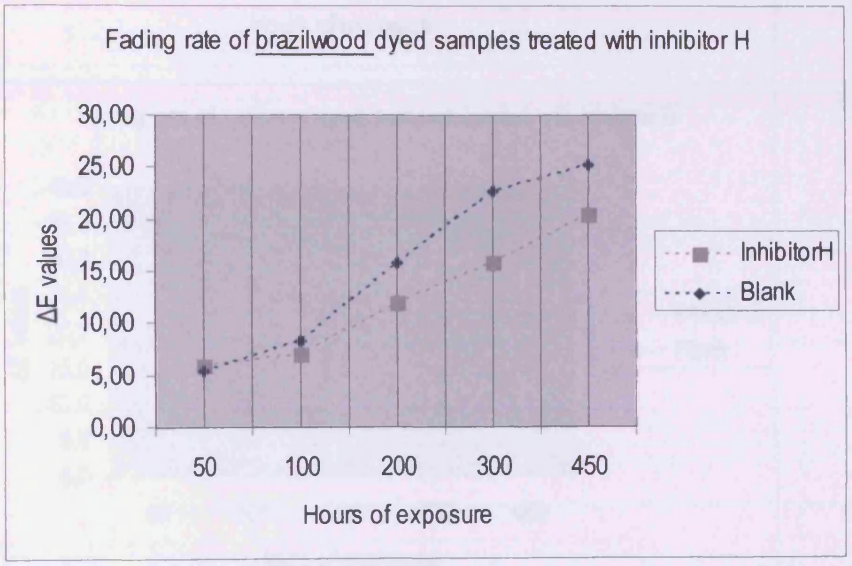


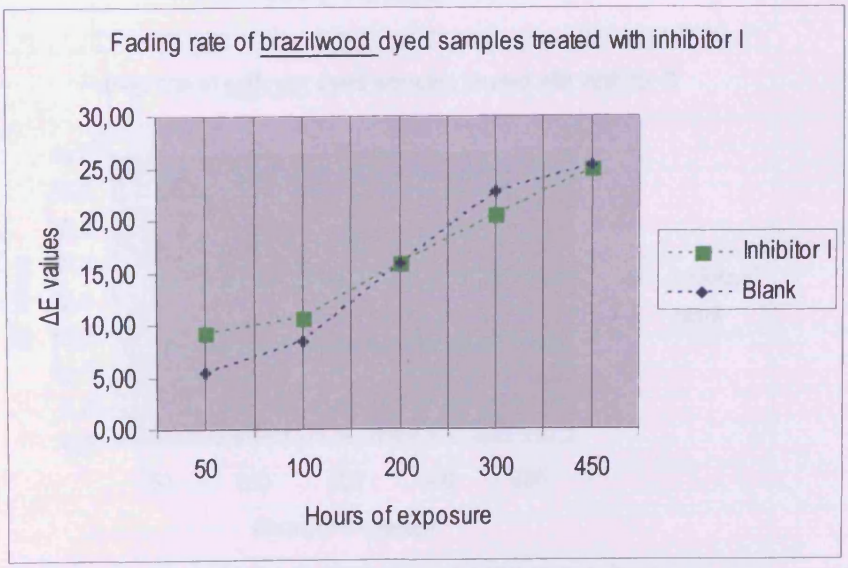

Fading rate of brazilwood dyed samples treated with inhibitor D
30,00
25,00
20,00
15,00
10,00
5,00
0,00
ΔE values
50
100
200
300
450
Hours of exposure
InhibitorD
Blank


Fading rate of brazilwood dyed samples treated with inhibitor E
30,00
25,00
20,00
15,00
10,00
5,00
0,00
ΔE values
50
100
200
300
450
Hours of exposure
InhibitorE
Blank

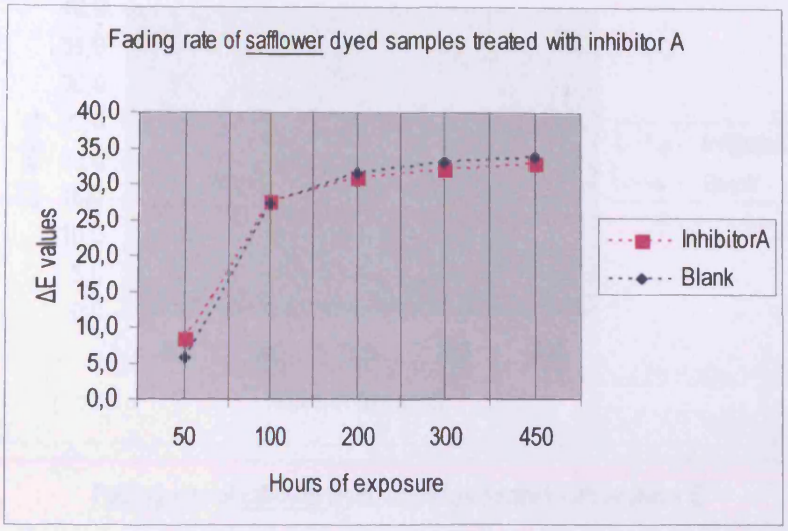

Fading rate of brazilwood dyed samples treated with inhibitor F
30,00
25,00
20,00
15,00
10,00
5,00
0,00
ΔE values
50
100
200
300
450
Hours of exposure
InhibitorF
Blank

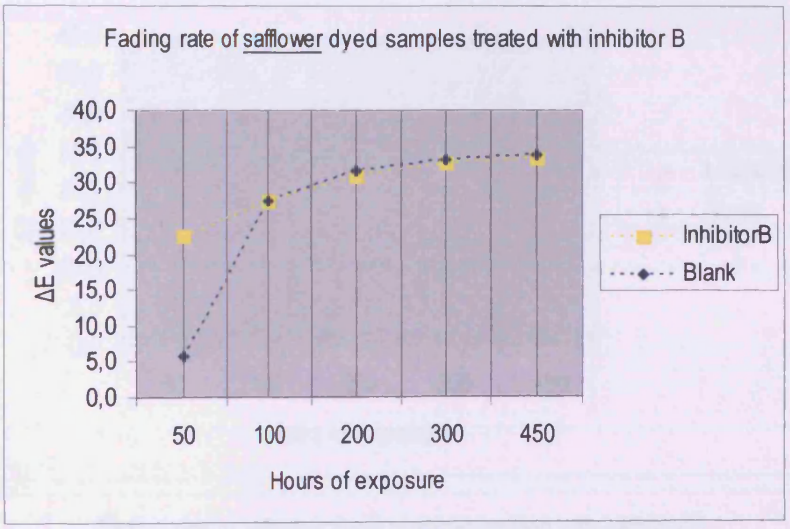

Fading rate of brazilwood dyed samples treated with inhibitor G
30,00
25,00
20,00
15,00
10,00
5,00
0,00
ΔE values
50
100
200
300
450
Hours of exposure
InhibitorG
Blank

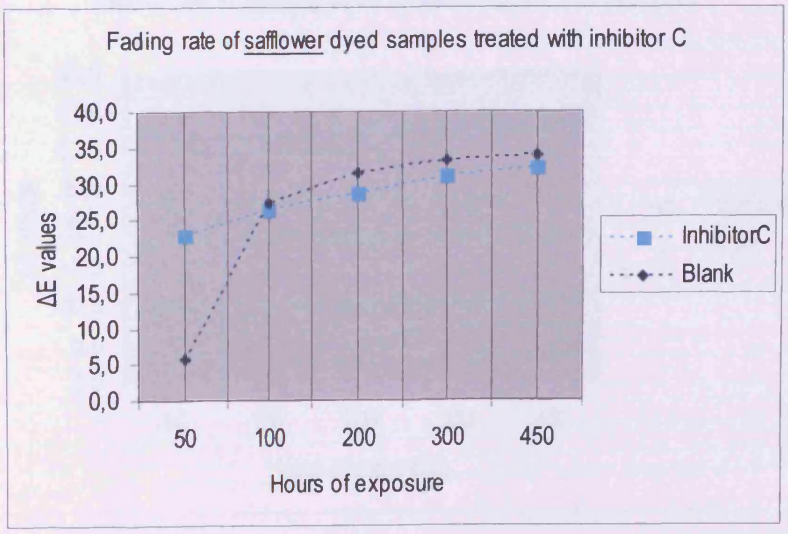

Fading rate of brazilwood dyed samples treated with inhibitor H
30,00
25,00
20,00
15,00
10,00
5,00
0,00
ΔE values
50
100
200
300
450
Hours of exposure
InhibitorH
Blank

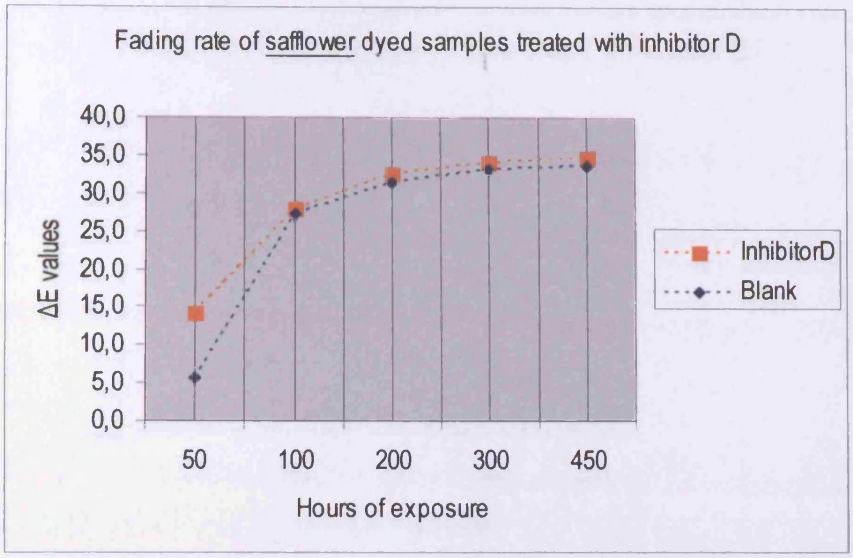

Fading rate of brazilwood dyed samples treated with inhibitor I
30,00
25,00
20,00
15,00
10,00
5,00
0,00
ΔE values
50
100
200
300
450
Hours of exposure
Inhibitor I
Blank

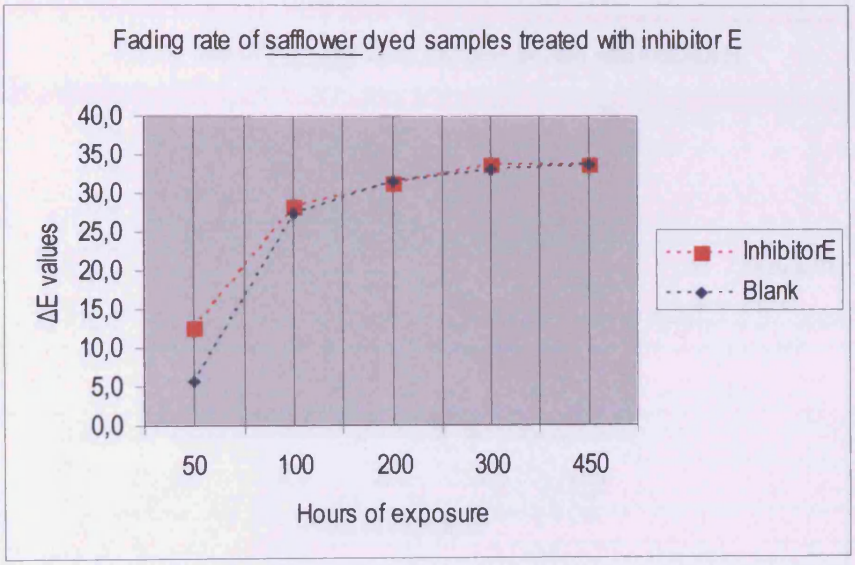
C.3.3 Fading rates of Safflower dyed samples

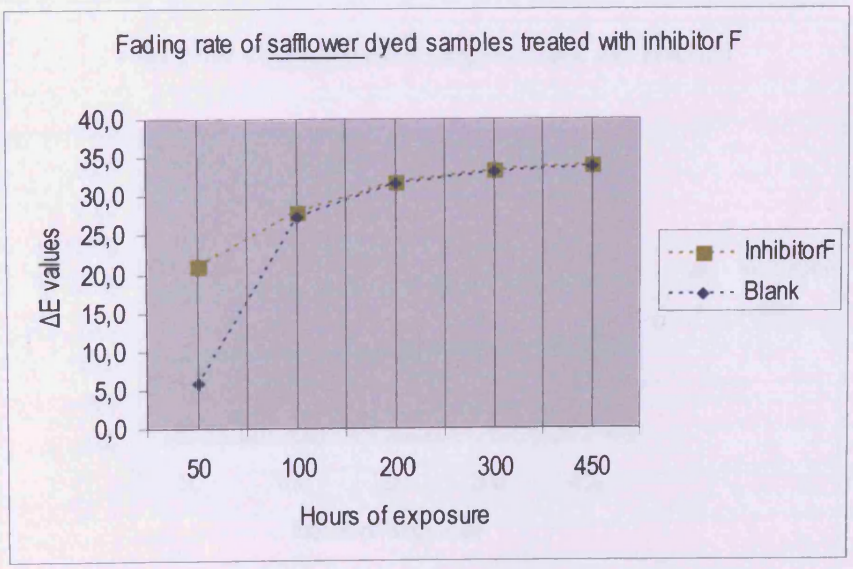


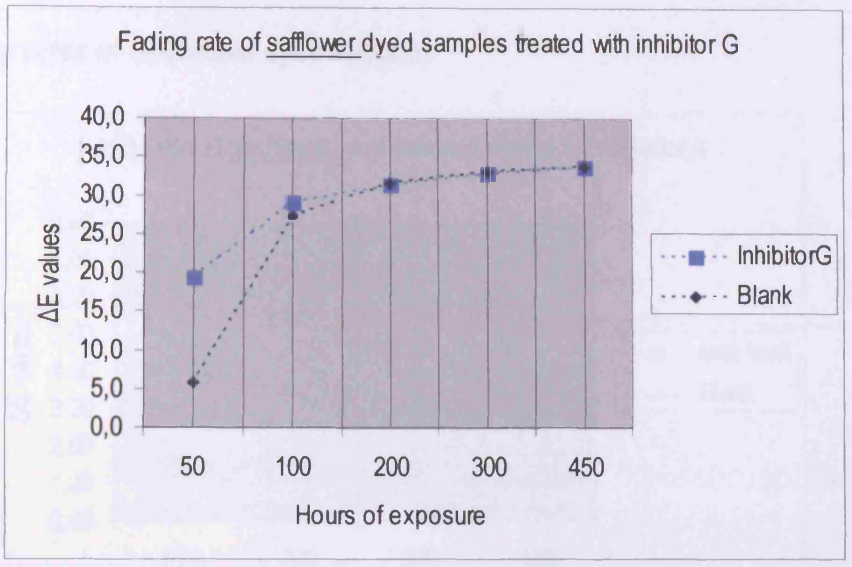


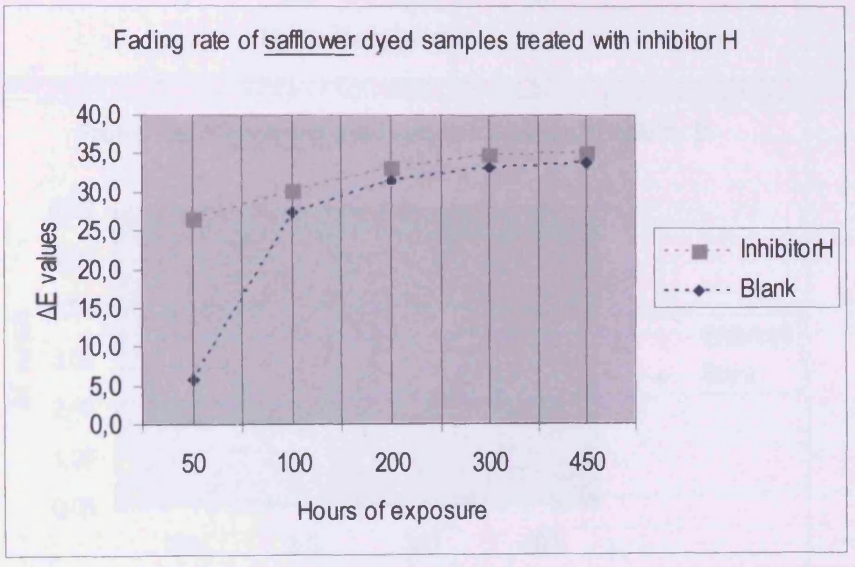


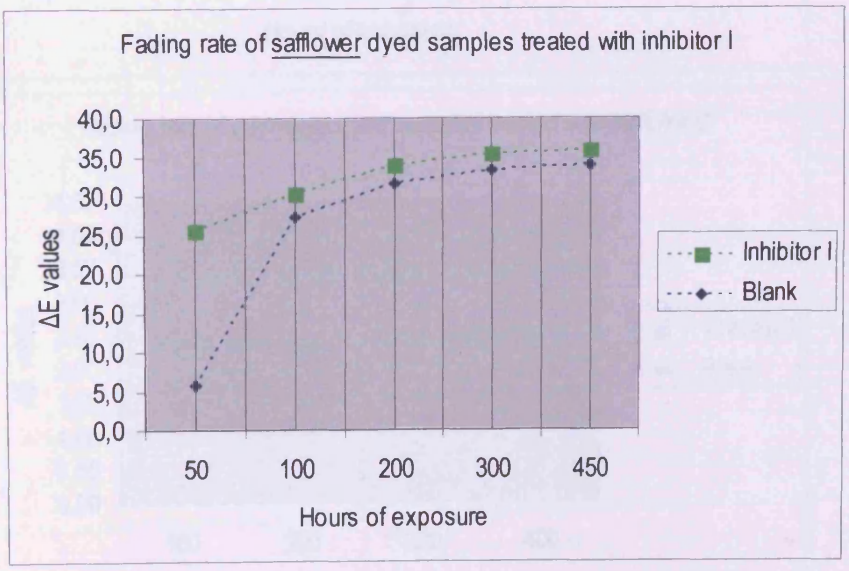

Fading rate of safflower dyed samples treated with inhibitor D
ΔE values
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
50
100
200
300
450
Hours of exposure
InhibitorD
Blank


Fading rate of safflower dyed samples treated with inhibitor E
ΔE values
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
50
100
200
300
450
Hours of exposure
InhibitorE
Blank

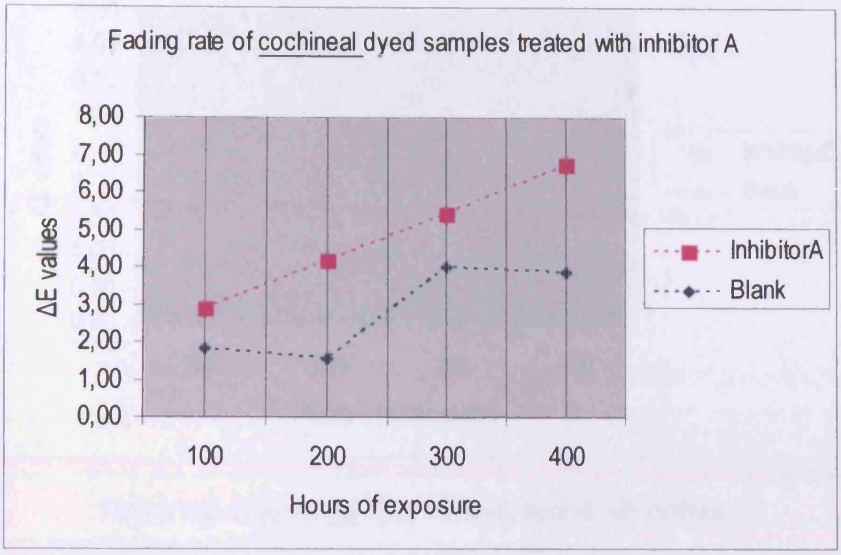

Fading rate of safflower dyed samples treated with inhibitor F
ΔE values
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
50
100
200
300
450
Hours of exposure
InhibitorF
Blank

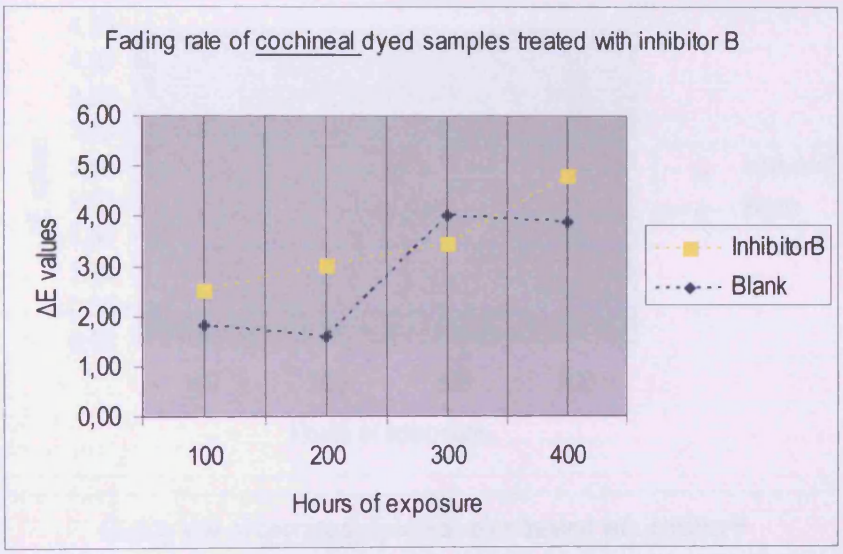

Fading rate of safflower dyed samples treated with inhibitor G
ΔE values
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
50
100
200
300
450
Hours of exposure
InhibitorG
Blank

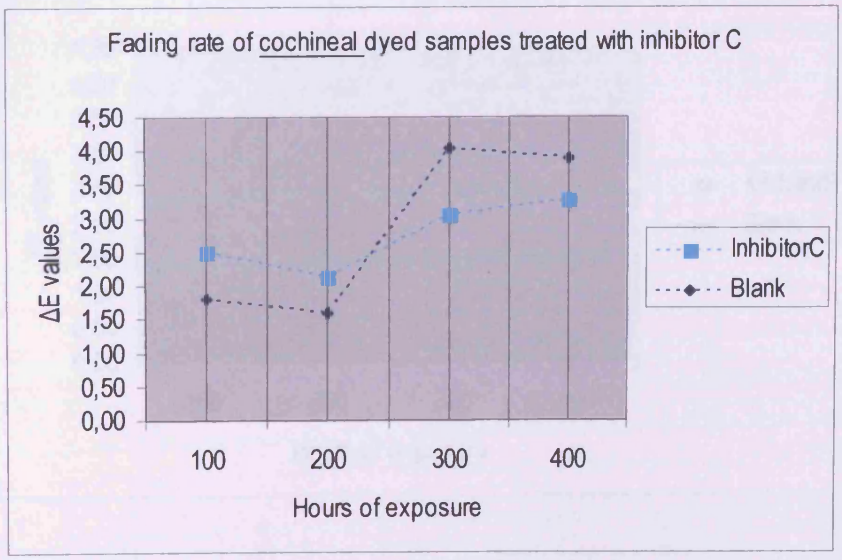

Fading rate of safflower dyed samples treated with inhibitor H
ΔE values
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
50
100
200
300
450
Hours of exposure
InhibitorH
Blank

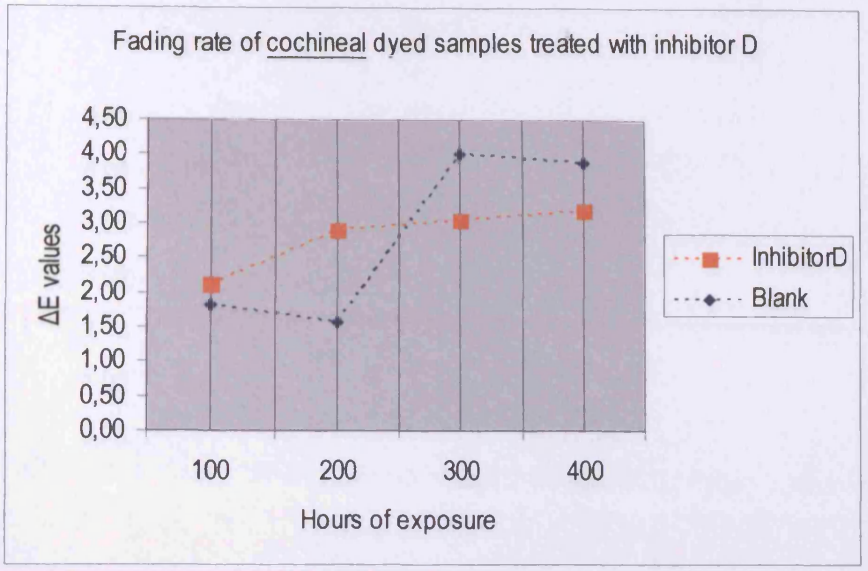

Fading rate of safflower dyed samples treated with inhibitor I
ΔE values
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
50
100
200
300
450
Hours of exposure
Inhibitor I
Blank

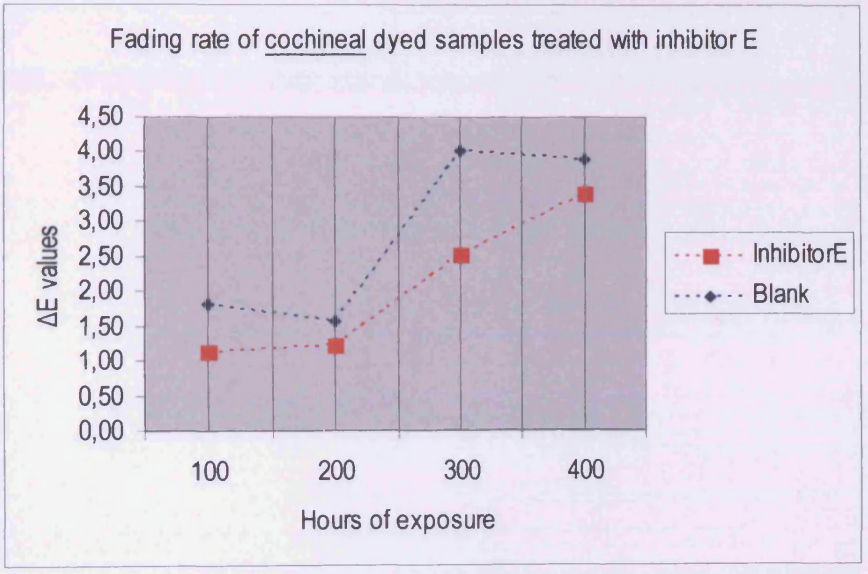
C.3.4 Fading rates of Cochineal dyed samples

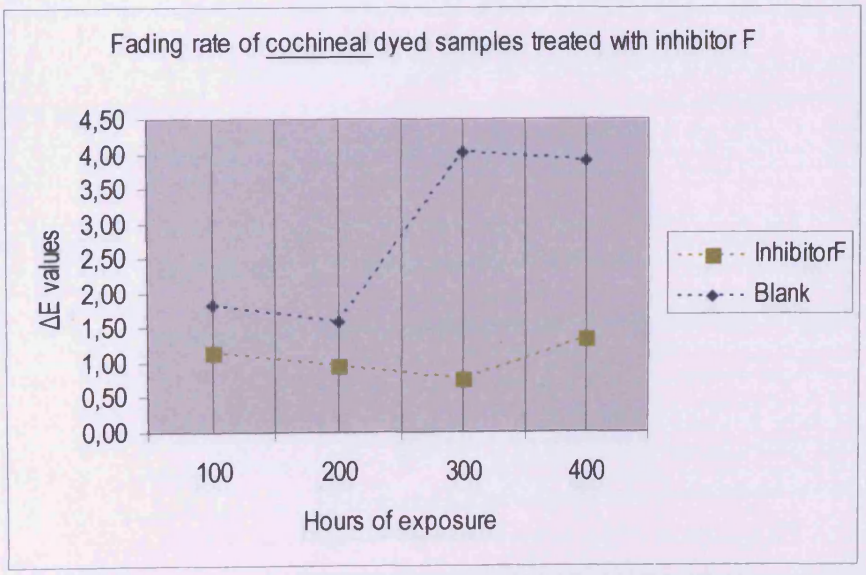


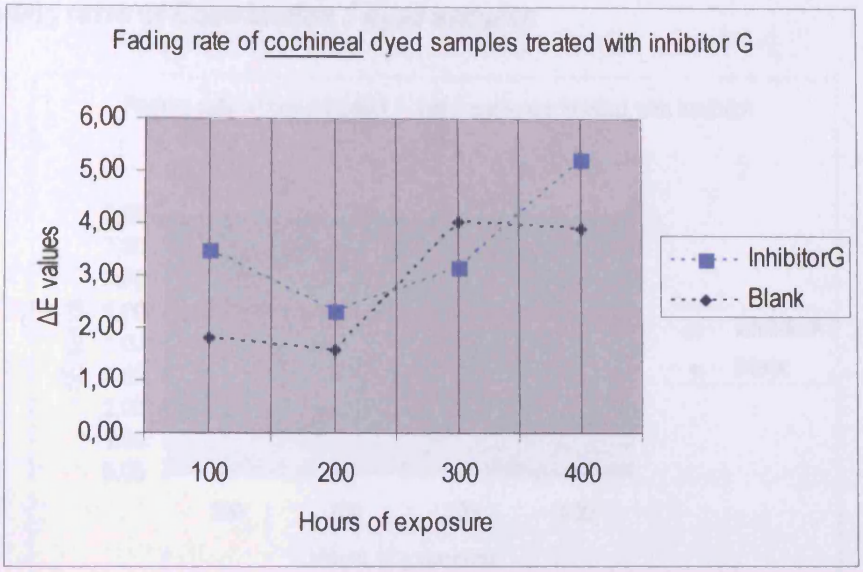


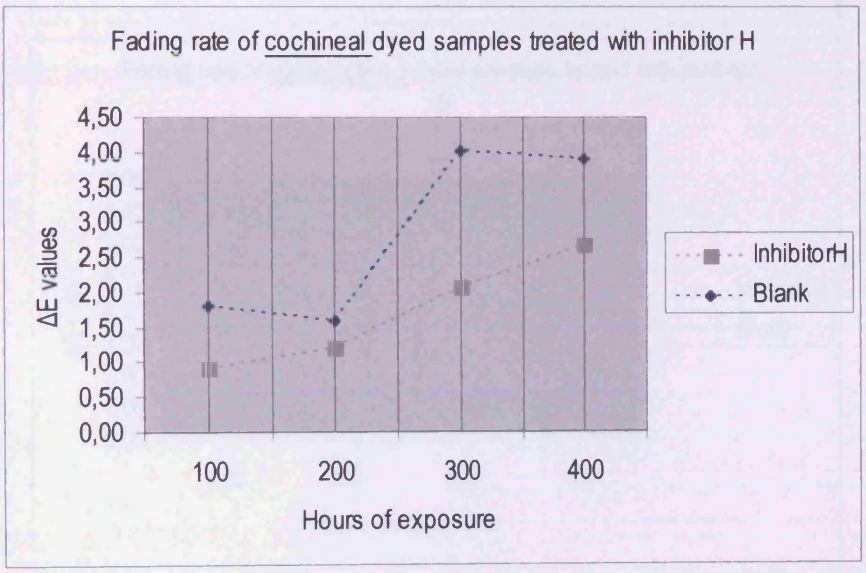


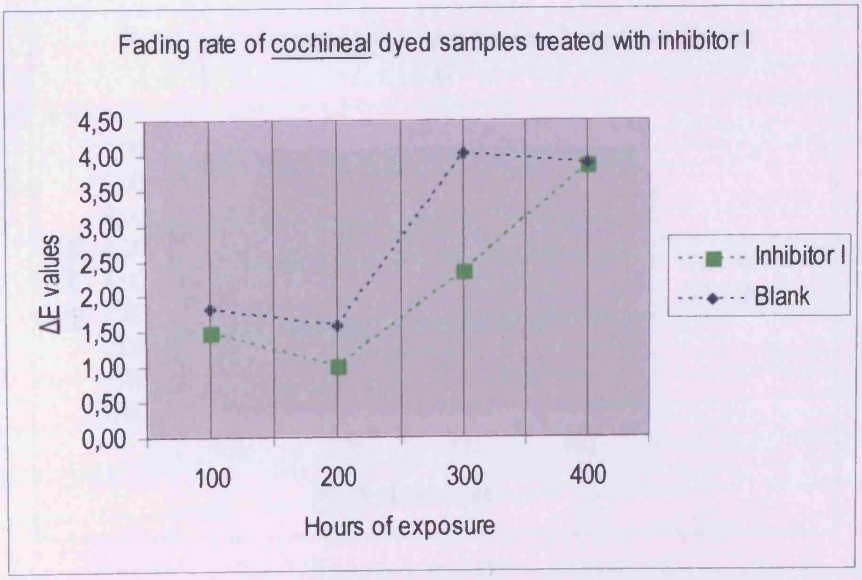

Fading rate of cochineal dyed samples treated with inhibitor D
ΔE values
4,50
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
100
200
300
400
Hours of exposure
InhibitorD
Blank


Fading rate of cochineal dyed samples treated with inhibitor E
ΔE values
4,50
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
100
200
300
400
Hours of exposure
InhibitorE
Blank

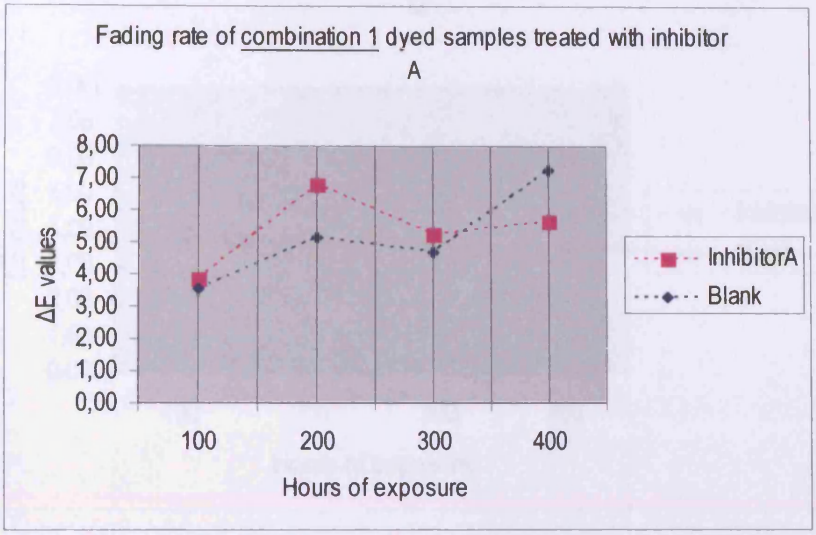

Fading rate of cochineal dyed samples treated with inhibitor F
ΔE values
4,50
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
100
200
300
400
Hours of exposure
InhibitorF
Blank

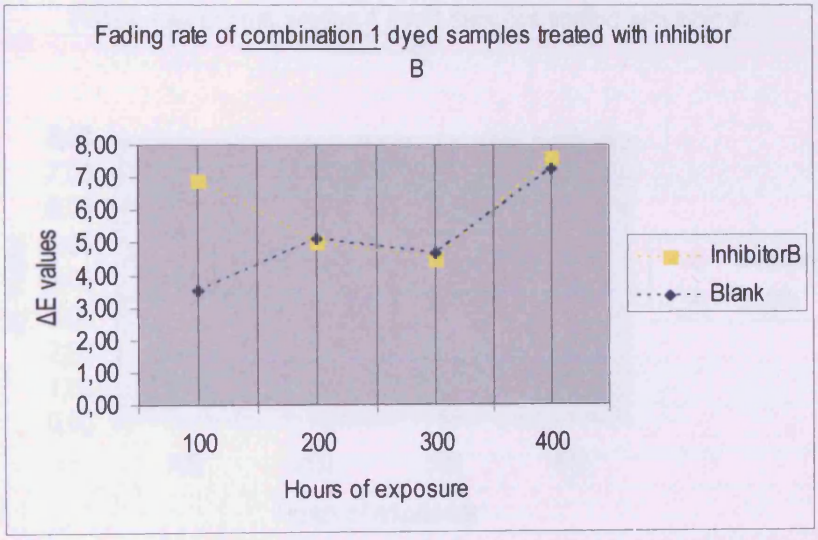

Fading rate of cochineal dyed samples treated with inhibitor G
6,00
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorG
Blank

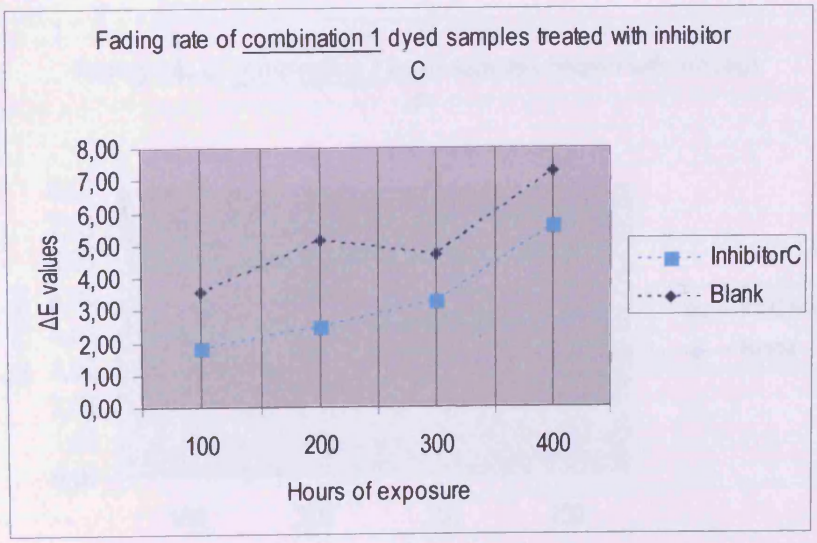

Fading rate of cochineal dyed samples treated with inhibitor H
4,50
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorH
Blank

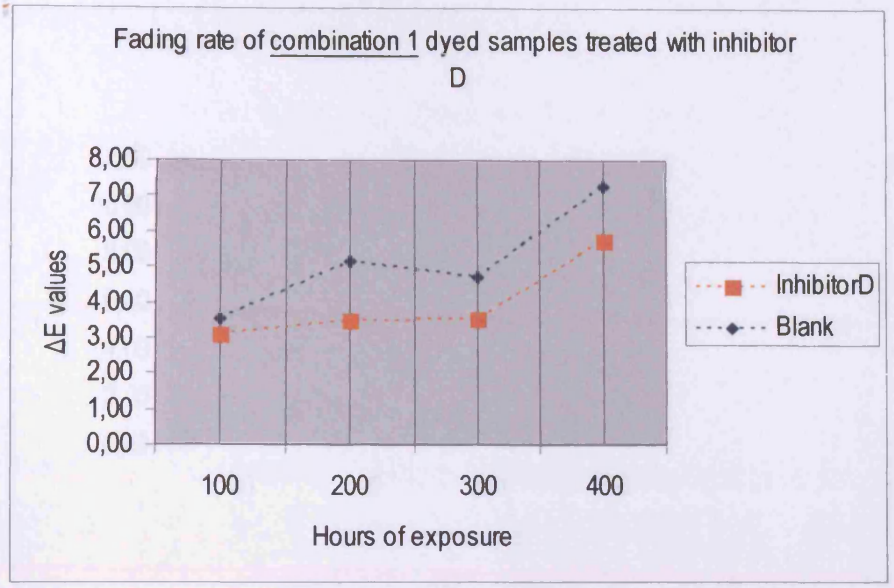

Fading rate of cochineal dyed samples treated with inhibitor I
4,50
4,00
3,50
3,00
2,50
2,00
1,50
1,00
0,50
0,00
ΔE values
100
200
300
400
Hours of exposure
Inhibitor I
Blank

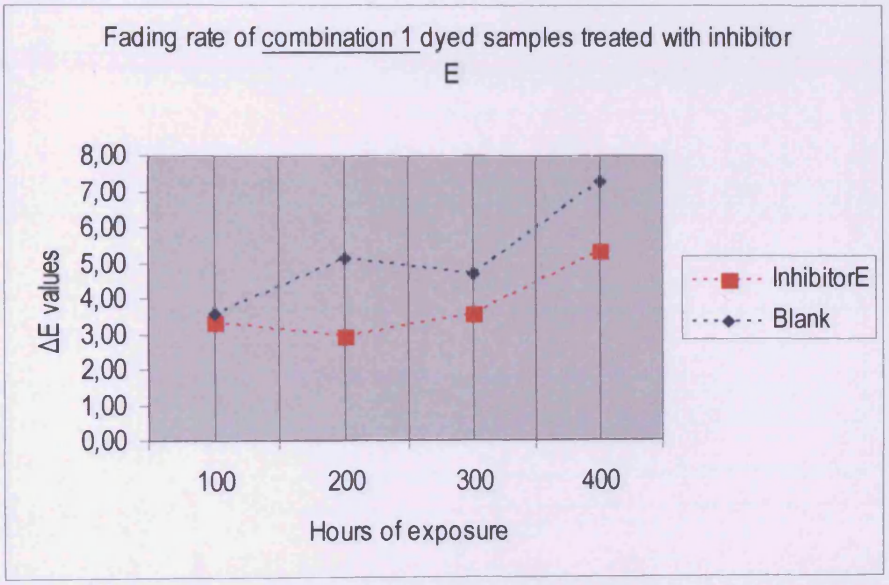
C.3.5 Fading rates of Combination 1 dyed samples

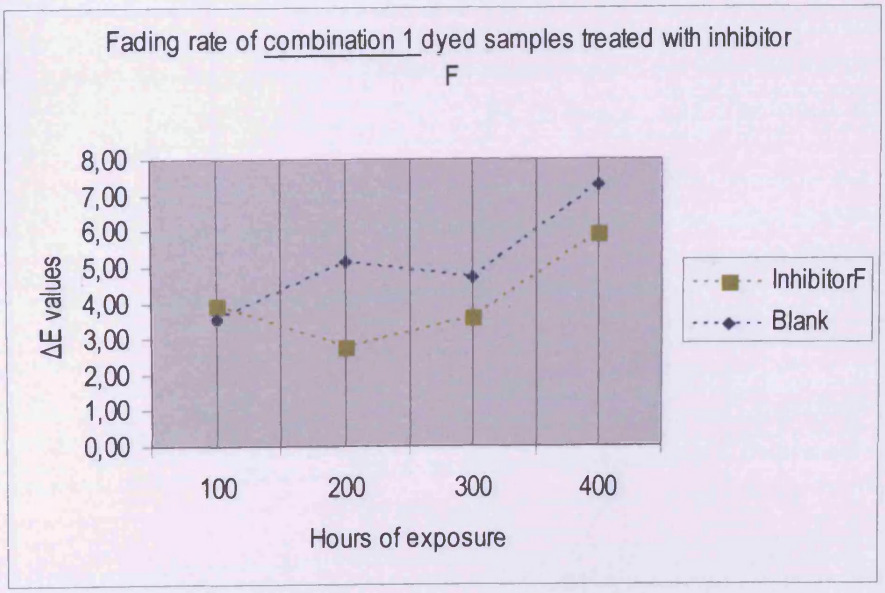


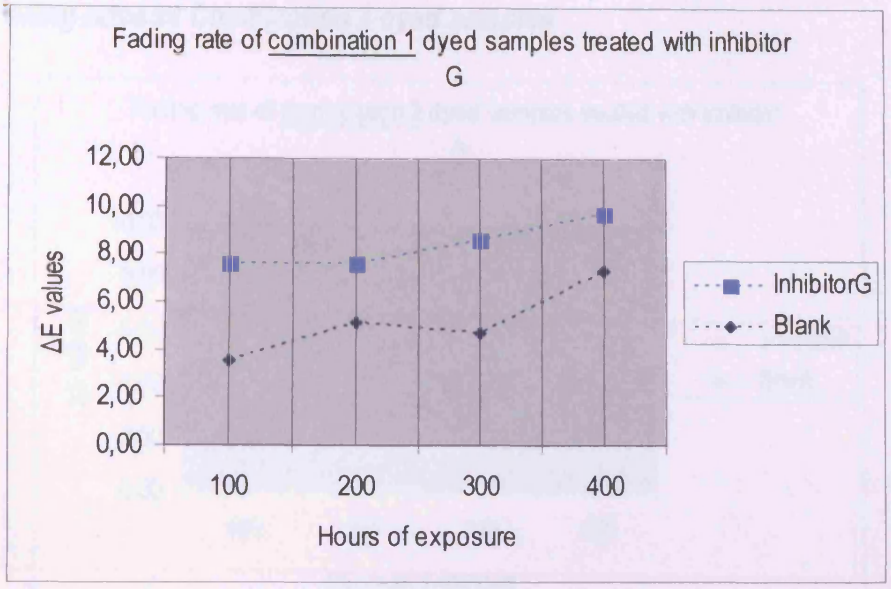


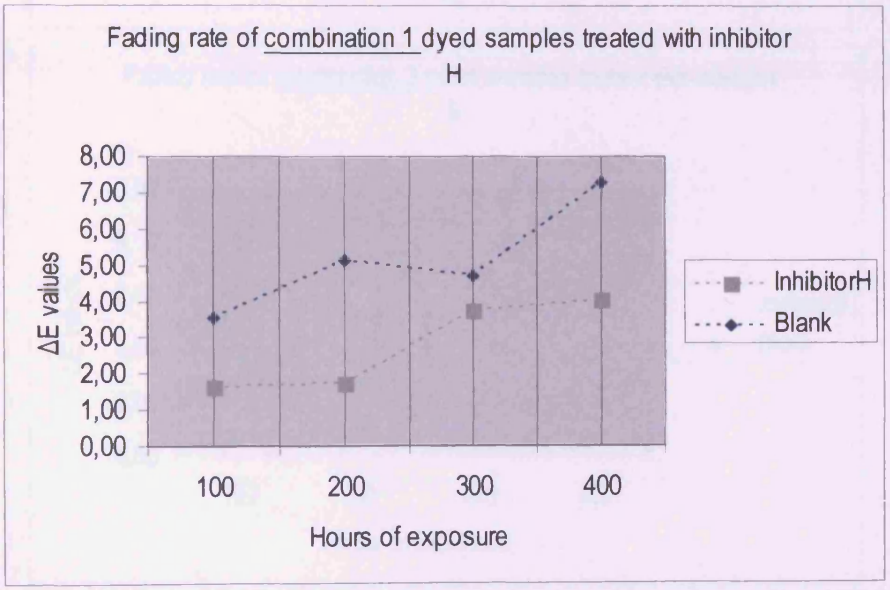


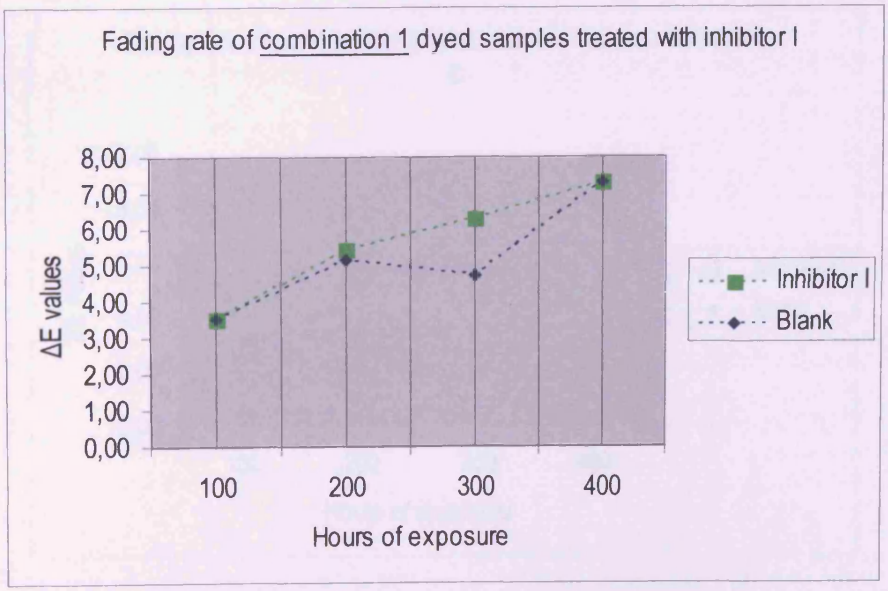

Fading rate of combination 1 dyed samples treated with inhibitor D
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorD
Blank


Fading rate of combination 1 dyed samples treated with inhibitor E
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorE
Blank

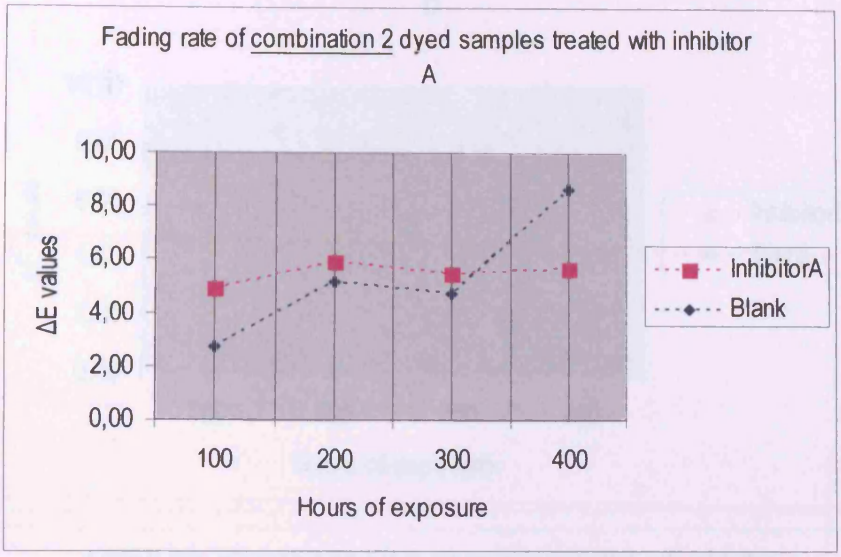

Fading rate of combination 1 dyed samples treated with inhibitor F
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorF
Blank

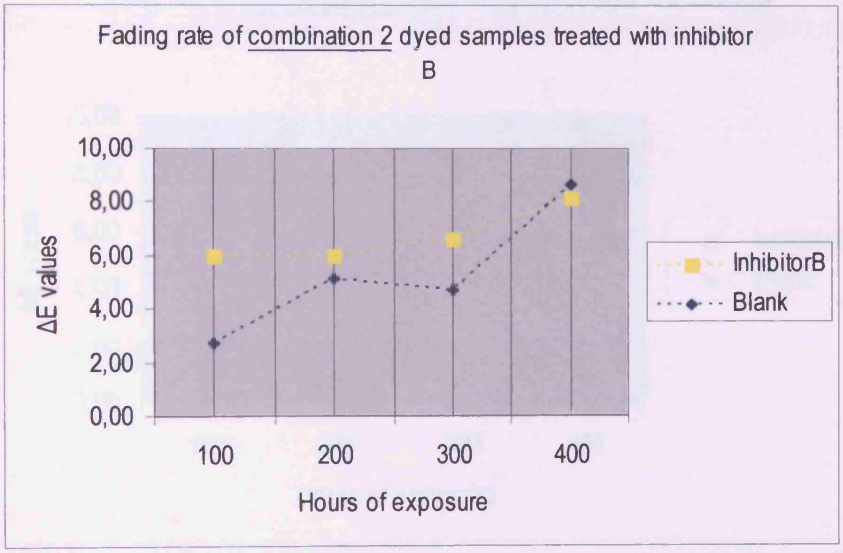

Fading rate of combination 1 dyed samples treated with inhibitor G
12,00
10,00
8,00
6,00
4,00
2,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorG
Blank

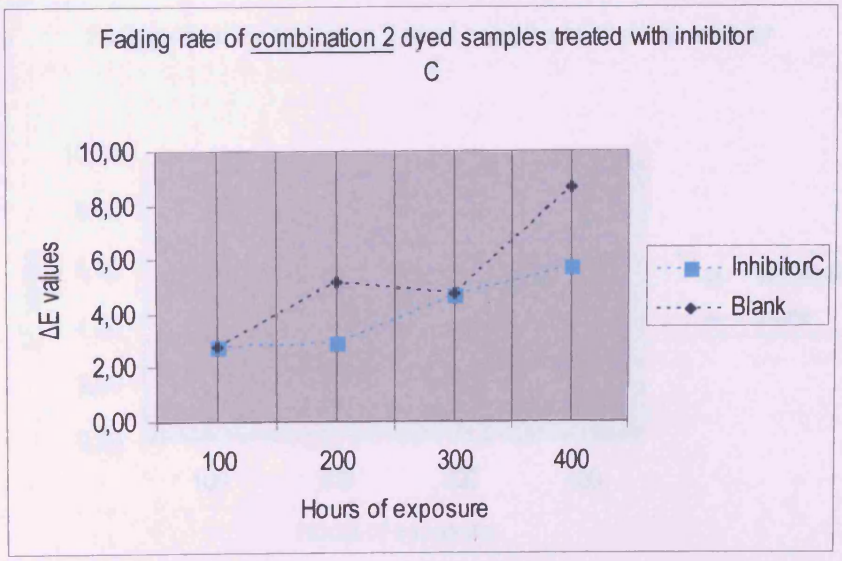

Fading rate of combination 1 dyed samples treated with inhibitor H
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorH
Blank

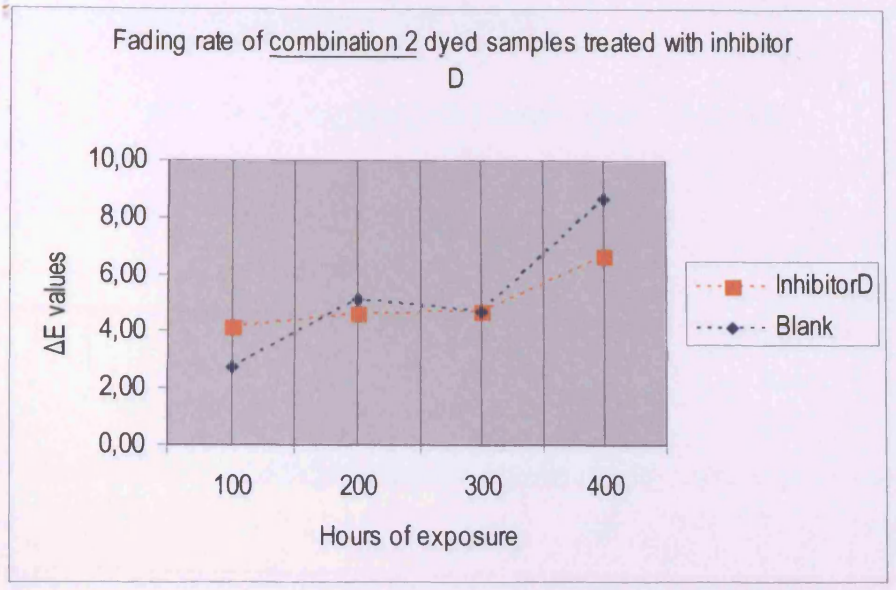

Fading rate of combination 1 dyed samples treated with inhibitor I
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
Inhibitor I
Blank

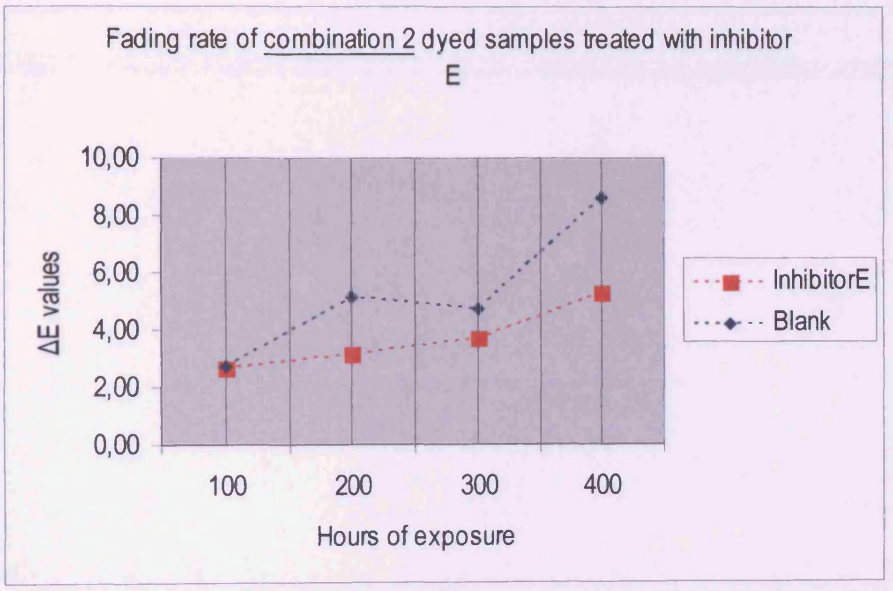
C.3.6 Fading rates of Combination 2 dyed samples

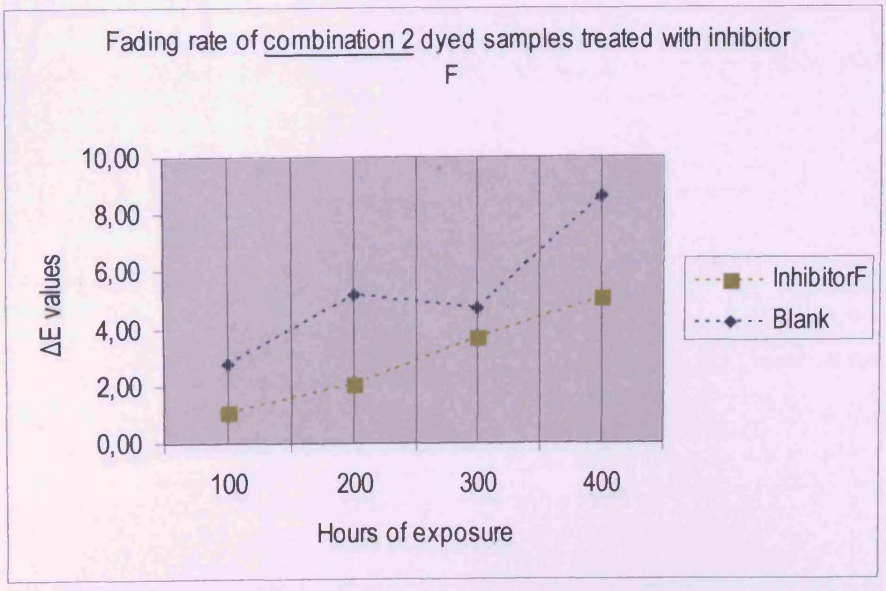


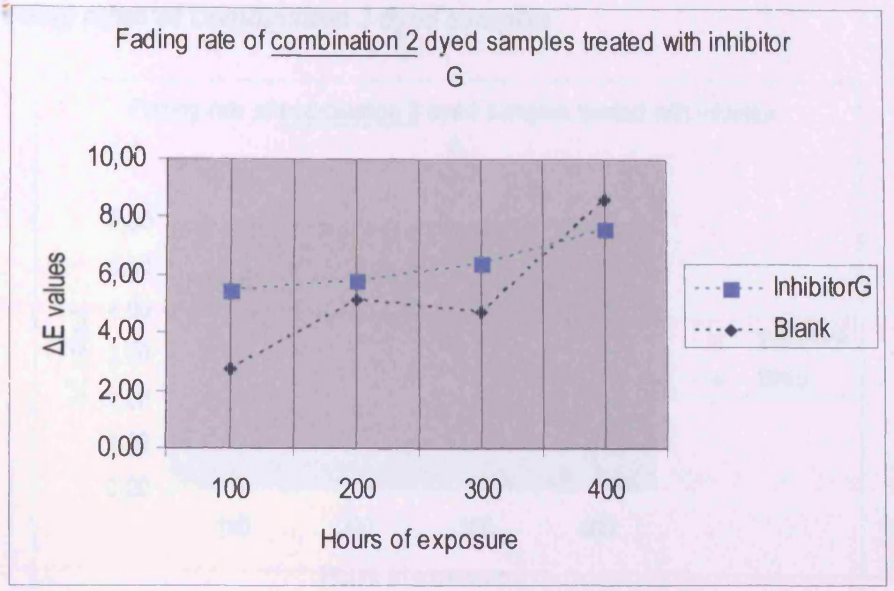


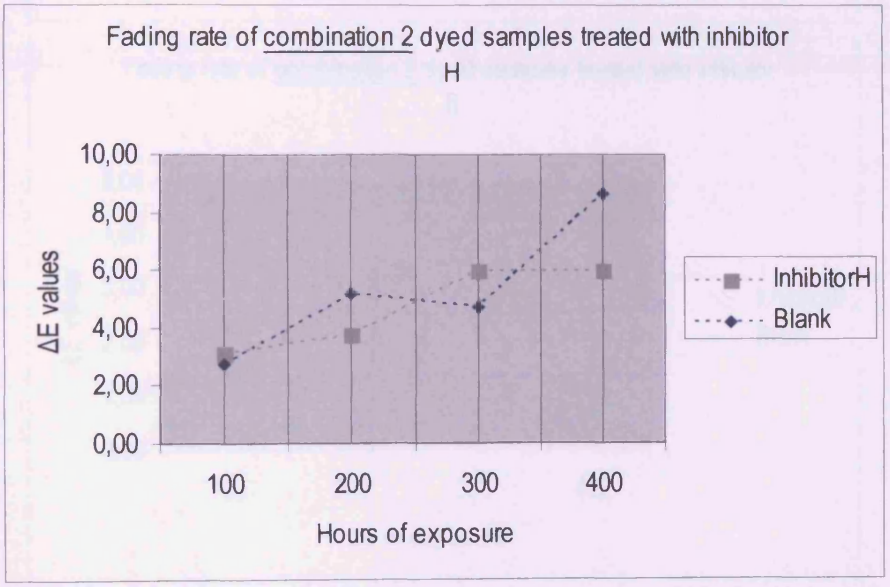


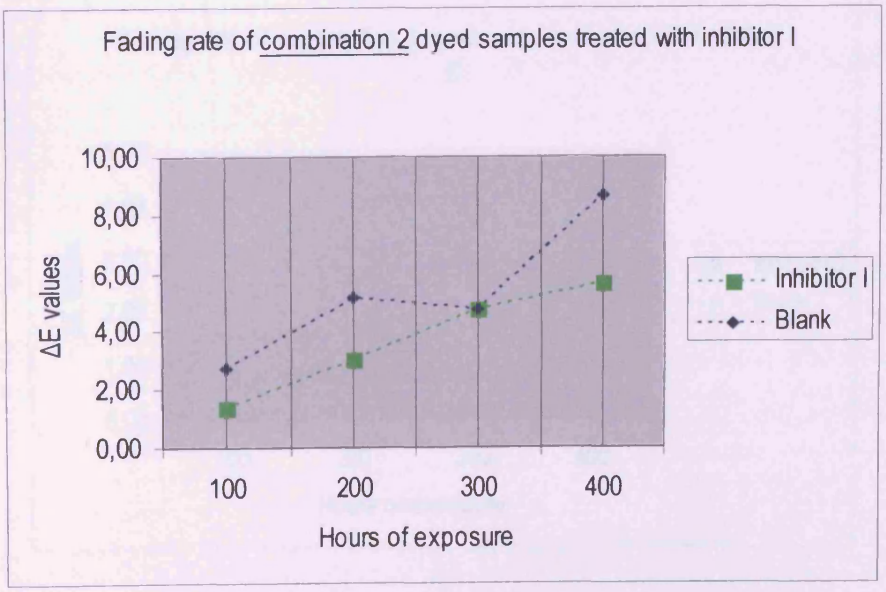

Fading rate of combination 2 dyed samples treated with inhibitor D
10,00
8,00
6,00
4,00
2,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorD
Blank


Fading rate of combination 2 dyed samples treated with inhibitor E
10,00
8,00
6,00
4,00
2,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorE
Blank

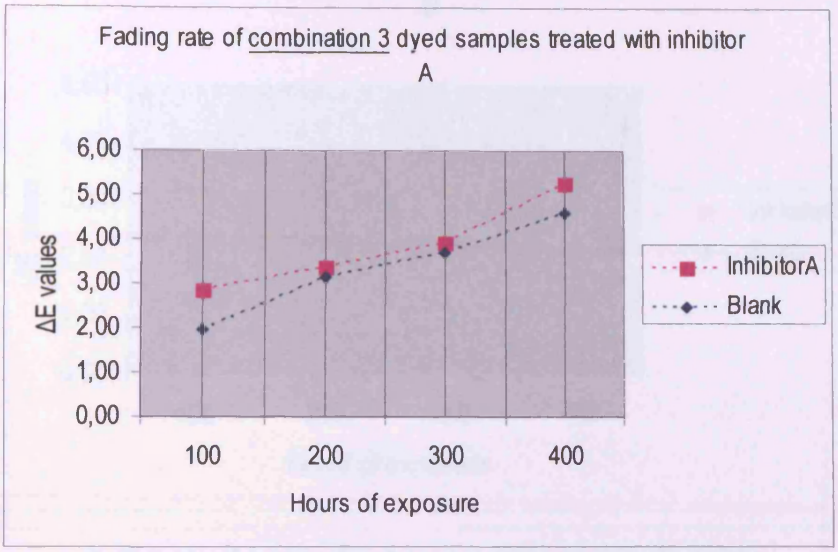

Fading rate of combination 2 dyed samples treated with inhibitor F
10,00
8,00
6,00
4,00
2,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorF
Blank

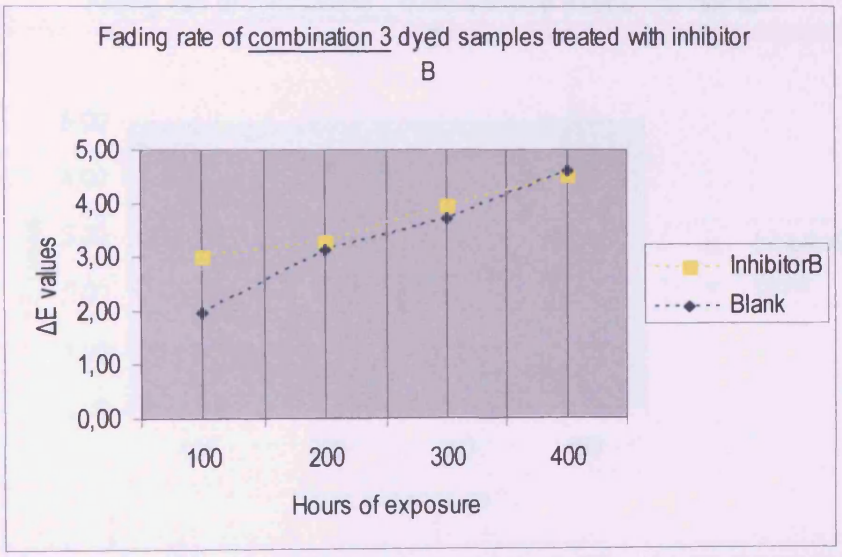

Fading rate of combination 2 dyed samples treated with inhibitor G
10,00
8,00
6,00
4,00
2,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorG
Blank

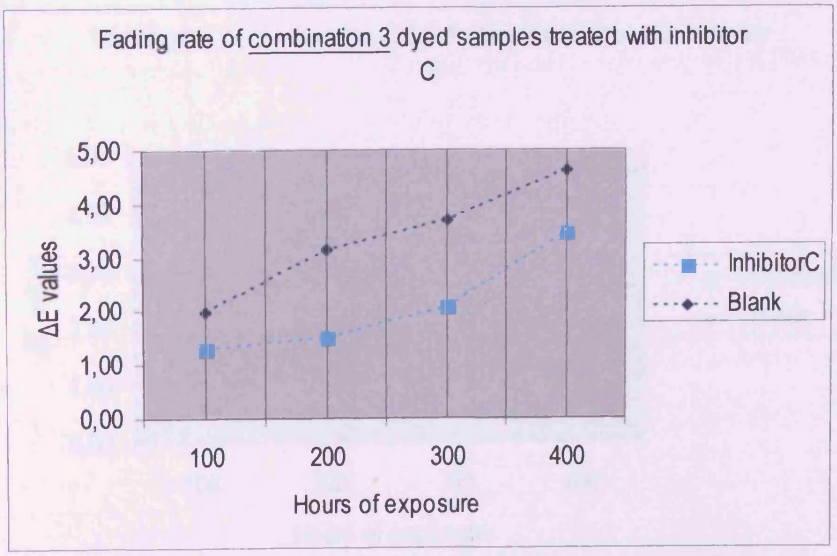

Fading rate of combination 2 dyed samples treated with inhibitor H
10,00
8,00
6,00
4,00
2,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorH
Blank

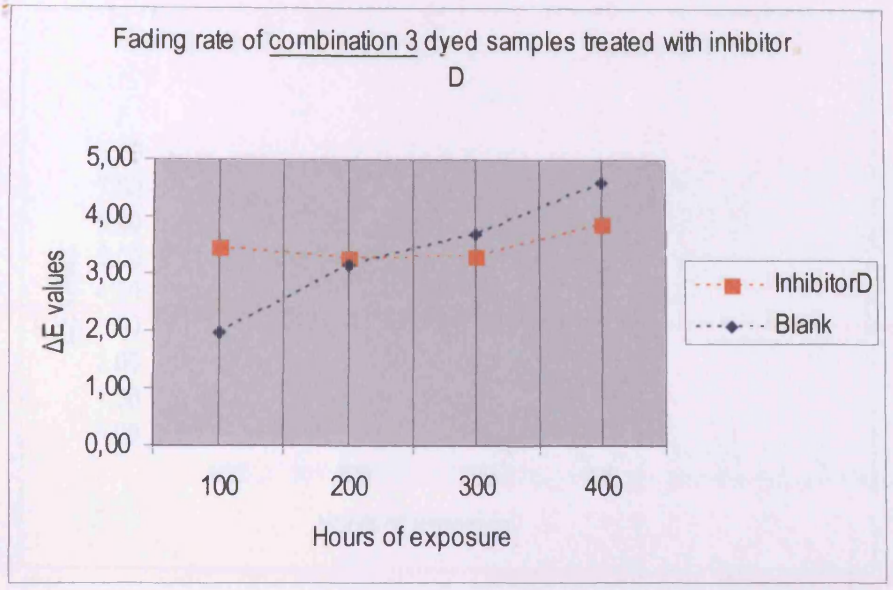

Fading rate of combination 2 dyed samples treated with inhibitor I
10,00
8,00
6,00
4,00
2,00
0,00
ΔE values
100
200
300
400
Hours of exposure
Inhibitor I
Blank

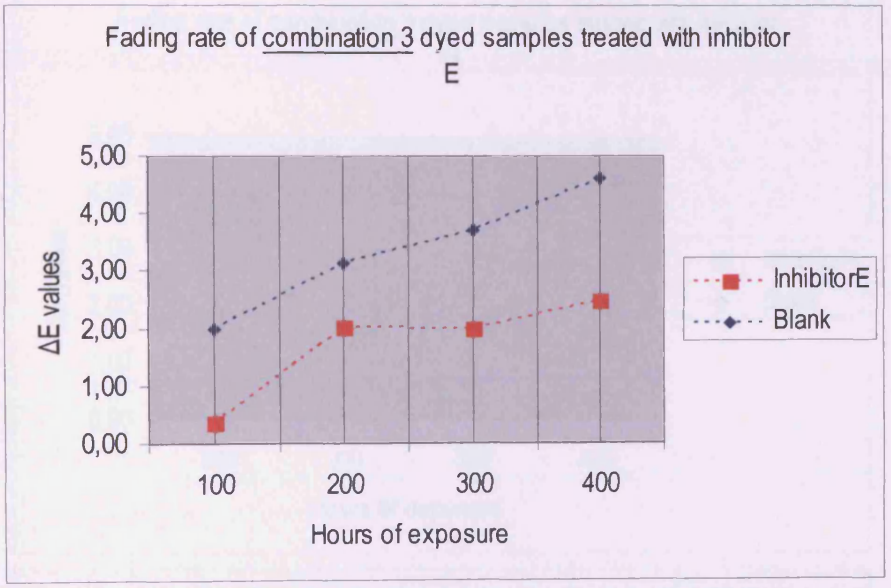
C.3.7 Fading rates of Combination 3 dyed samples

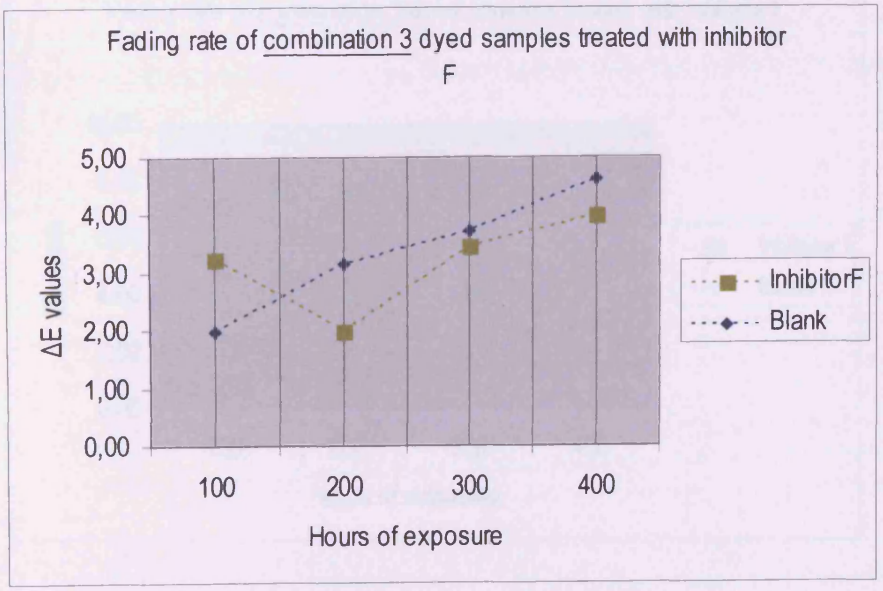


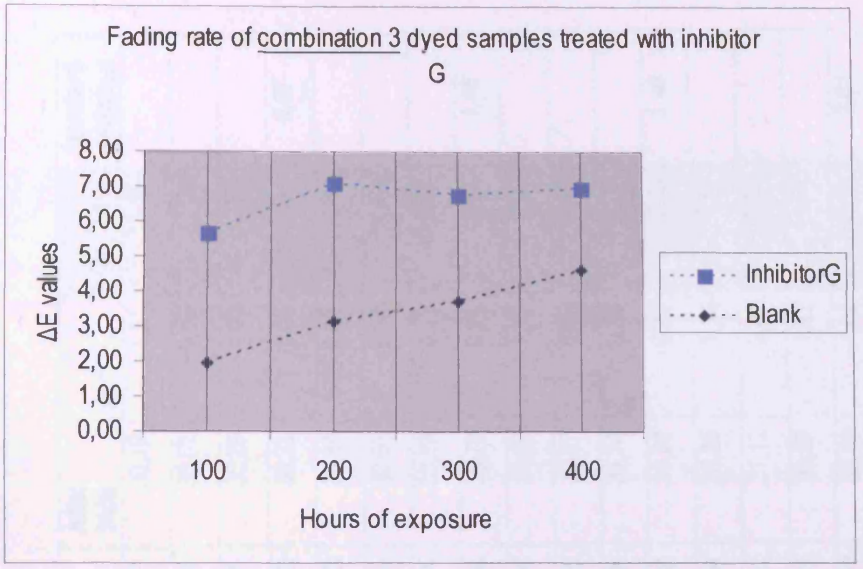


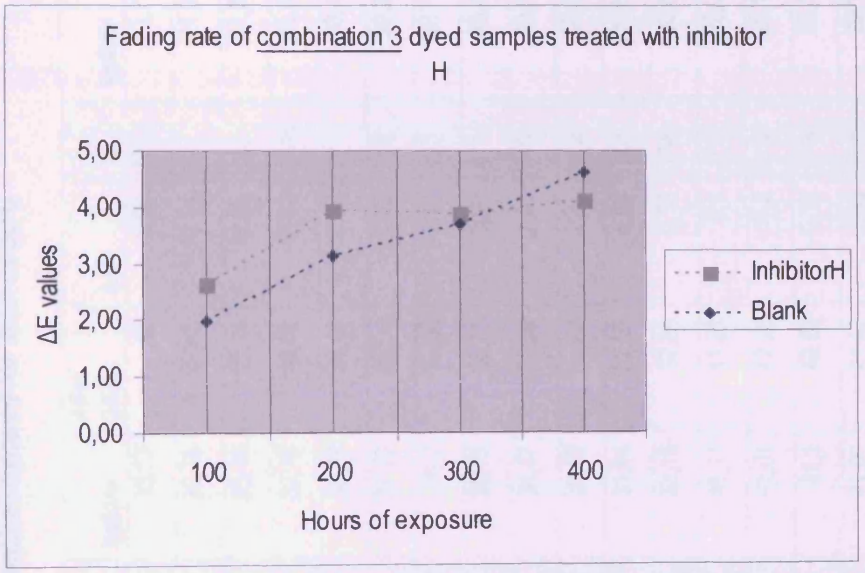


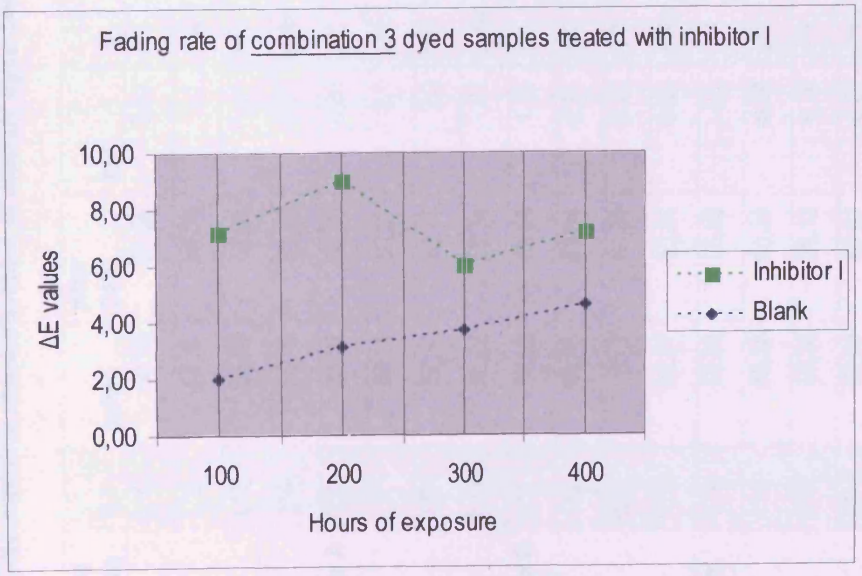

Fading rate of combination 3 dyed samples treated with inhibitor D
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorD
Blank


Fading rate of combination 3 dyed samples treated with inhibitor E
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorE
Blank


Fading rate of combination 3 dyed samples treated with inhibitor F
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorF
Blank


Fading rate of combination 3 dyed samples treated with inhibitor G
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorG
Blank


Fading rate of combination 3 dyed samples treated with inhibitor H
5,00
4,00
3,00
2,00
1,00
0,00
ΔE values
100
200
300
400
Hours of exposure
InhibitorH
Blank


Fading rate of combination 3 dyed samples treated with inhibitor I
10,00
8,00
6,00
4,00
2,00
0,00
ΔE values
100
200
300
400
Hours of exposure
Inhibitor I
Blank

C.4 Colourimetric measurements of samples exposed at 50°C

C.4.1 Colourimetric measurements of Madder dyed samples exposed for 240h at 50°C

Treated samples	L*	before	After 240h	ΔL*	a*	before	After 240h	Δa*	b*	before	After 240h	Δb*	ΔE	Standard deviation
Blank	L*1	50,92	51,55	0,63	a*1	35,03	45	9,97	b*1	31,73	30,19	-1,54	10,11	
	L*2	55,39	54,39	-1	a*2	32,75	43,89	11,14	b*2	31,04	30,52	-0,52	11,20	
	L*3	55,68	54,04	-1,64	a*3	33,48	45,14	11,66	b*3	31,38	30,29	-1,09	11,83	
	L*Av	54,00	53,33	-0,67	a*Av	33,75	44,68	10,92	b*Av	31,38	30,33	-1,05	11,04	*0,87*
Inhibitor A	L*1	58,27	58,35	0,08	a*1	38,77	39,49	0,72	b*1	30,43	30,88	0,45	0,85	
	L*2	59,11	59,21	0,1	a*2	37,77	39,09	1,32	b*2	30,24	30,63	0,39	1,38	
	L*3	57,57	60,47	2,9	a*3	39,7	37,56	-2,14	b*3	30,71	30,59	-0,12	3,61	
	L*Av	58,32	59,34	1,03	a*Av	38,75	38,71	-0,03	b*Av	30,46	30,70	0,24	1,95	*1,46*
Inhibitor B	L*1	62,03	63,88	1,85	a*1	34,47	32,56	-1,91	b*1	30,58	31,69	1,11	2,88	
	L*2	65,98	63,04	-2,94	a*2	30,13	33	2,87	b*2	30,55	30,97	0,42	4,13	
	L*3	65,1	64,61	-0,49	a*3	31,84	32,52	0,68	b*3	30,86	31,74	0,88	1,22	
	L*Av	64,37	63,84	-0,53	a*Av	32,15	32,69	0,55	b*Av	30,66	31,47	0,80	2,74	*1,46*
Inhibitor C	L*1	55,85	55,65	-0,2	a*1	41,11	41,21	0,1	b*1	29,24	30,38	1,14	1,16	
	L*2	55,58	55,24	-0,34	a*2	41,01	42,21	1,2	b*2	29,11	31,12	2,01	2,37	
	L*3	55,36	56,12	0,76	a*3	41,1	40,98	-0,12	b*3	29,15	30,57	1,42	1,62	
	L*Av	55,60	55,67	0,07	a*Av	41,07	41,47	0,39	b*Av	29,17	30,69	1,52	1,71	*0,61*
Inhibitor D	L*1	57,12	55,54	-1,58	a*1	39,23	40,09	0,86	b*1	31,69	30,97	-0,72	1,94	
	L*2	56,27	56,34	0,07	a*2	40,78	39	-1,78	b*2	31,82	30,68	-1,14	2,11	
	L*3	56,04	56,25	0,21	a*3	39,87	39,91	0,04	b*3	31,71	30,54	-1,17	1,19	
	L*Av	56,48	56,04	-0,43	a*Av	39,96	39,67	-0,29	b*Av	31,74	30,73	-1,01	1,75	*0,49*

Treated samples	L*	before	After 240h	ΔL*	a*	before	After 240h	Δa*	b*	before	After 240h	Δb*	ΔE	Standard deviation
Inhibitor E	L*1	54,96	54,1	-0,86	a*1	41,76	42,53	0,77	b*1	31,74	31,88	0,14	1,16	
	L*2	55,94	54,94	-1	a*2	40,23	41,76	1,53	b*2	30,88	32,03	1,15	2,16	
	L*3	54,4	55,77	1,37	a*3	42,6	40,67	-1,93	b*3	31,86	30,99	-0,87	2,52	
	L*Av	55,10	54,94	-0,16	a*Av	41,53	41,65	0,12	b*Av	31,49	31,63	0,14	1,95	*0,70*
Inhibitor F	L*1	57,27	57,7	0,43	a*1	39,26	39,69	0,43	b*1	30,87	31,47	0,6	0,85	
	L*2	58	56,86	-1,14	a*2	38,35	39,61	1,26	b*2	30,99	31,61	0,62	1,81	
	L*3	57,68	57,6	-0,08	a*3	39,34	39,06	-0,28	b*3	31,64	30,96	-0,68	0,74	
	L*Av	57,65	57,39	-0,26	a*Av	38,98	39,45	0,47	b*Av	31,17	31,35	0,18	1,13	*0,59*
Inhibitor G	L*1	59,51	59,05	-0,46	a*1	36,48	36,75	0,27	b*1	28,09	30,34	2,25	2,31	
	L*2	60,49	59,2	-1,29	a*2	35	37,02	2,02	b*2	27,85	30,28	2,43	3,41	
	L*3	61,65	59,98	-1,67	a*3	34,15	35,56	1,41	b*3	27,78	30,12	2,34	3,20	
	L*Av	60,55	59,41	-1,14	a*Av	35,21	36,44	1,23	b*Av	27,91	30,25	2,34	2,98	*0,58*
Inhibitor H	L*1	53,66	53,83	0,17	a*1	43,43	42,74	-0,69	b*1	30,85	30,87	0,02	0,71	
	L*2	53,54	54,04	0,5	a*2	43,12	43,6	0,48	b*2	30,84	30,86	0,02	0,69	
	L*3	54,06	54,04	-0,02	a*3	43,49	42,34	-1,15	b*3	30,47	30,59	0,12	1,16	
	L*Av	53,75	53,97	0,22	a*Av	43,35	42,89	-0,45	b*Av	30,72	30,77	0,05	0,85	*0,26*
Inhibitor I	L*1	61,4	63,95	2,55	a*1	35,03	33,82	-1,21	b*1	31,73	31,46	-0,27	2,84	
	L*2	63,93	62,33	-1,6	a*2	32,75	34,43	1,68	b*2	31,04	31,57	0,53	2,38	
	L*3	62,94	62,86	-0,08	a*3	33,48	33,89	0,41	b*3	31,38	30,65	-0,73	0,84	
	L*Av	62,76	63,05	0,29	a*Av	33,75	34,05	0,29	b*Av	31,38	31,23	-0,16	2,02	*1,05*

C.4.2 Colourimetric measurements of Madder dyed samples exposed for 400h at 50°C

Treated samples	L*	before	After 400h	ΔL*	a*	before	After 400h	Δa*	b*	before	After 400h	Δb*	ΔE	Standard deviation
Blank	L*1	50,92	52,26	1,34	a*1	35,03	45,06	10,03	b*1	31,73	30,52	-1,21	10,19	
	L*2	55,39	53,17	-2,22	a*2	32,75	44,81	12,06	b*2	31,04	30,61	-0,43	12,27	
	L*3	55,68	51,89	-3,79	a*3	33,48	45,01	11,53	b*3	31,38	30,34	-1,04	12,18	
	L*Av	54,00	52,44	-1,56	a*Av	33,75	44,96	11,21	b*Av	31,38	30,49	-0,89	11,55	*1,18*
Inhibitor A	L*1	58,27	59,41	1,14	a*1	38,77	39,04	0,27	b*1	30,43	31,24	0,81	1,42	
	L*2	59,11	60,47	1,36	a*2	37,77	37,9	0,13	b*2	30,24	30,71	0,47	1,44	
	L*3	57,57	61,58	4,01	a*3	39,7	37,82	-1,88	b*3	30,71	31,03	0,32	4,44	
	L*Av	58,32	60,49	2,17	a*Av	38,75	38,25	-0,49	b*Av	30,46	30,99	0,53	2,44	*1,74*
Inhibitor B	L*1	62,03	65,17	3,14	a*1	34,47	31,48	-2,99	b*1	30,58	30,94	0,36	4,35	
	L*2	65,98	66,48	0,5	a*2	30,13	30,65	0,52	b*2	30,55	31,31	0,76	1,05	
	L*3	65,1	66,42	1,32	a*3	31,84	29,92	-1,92	b*3	30,86	30,82	-0,04	2,33	
	L*Av	64,37	66,02	1,65	a*Av	32,15	30,68	-1,46	b*Av	30,66	31,02	0,36	2,58	*1,67*
Inhibitor C	L*1	55,85	55,37	-0,48	a*1	41,11	41,63	0,52	b*1	29,24	31,06	1,82	1,95	
	L*2	55,58	57,11	1,53	a*2	41,01	40,36	-0,65	b*2	29,11	30,68	1,57	2,29	
	L*3	55,36	57,01	1,65	a*3	41,1	41,43	0,33	b*3	29,15	30,9	1,75	2,43	
	L*Av	55,597	56,497	0,900	a*Av	41,073	41,140	0,067	b*Av	29,167	30,880	1,713	2,22	*0,24*
Inhibitor D	L*1	57,12	57,11	-0,01	a*1	39,23	39,02	-0,21	b*1	31,69	30,66	-1,03	1,05	
	L*2	56,27	56,38	0,11	a*2	40,78	39,8	-0,98	b*2	31,82	31,16	-0,66	1,19	
	L*3	56,04	58,83	2,79	a*3	39,87	37,47	-2,4	b*3	31,71	30,35	-1,36	3,92	
	L*Av	56,48	57,44	0,96	a*Av	39,96	38,76	-1,20	b*Av	31,74	30,72	-1,02	2,05	*1,62*

Treated samples	L*	before	After 400h	ΔL*	a*	before	After 400h	Δa*	b*	before	After 400h	Δb*	ΔE	Standard deviation
Inhibitor E	L*1	54,96	54,65	-0,31	a*1	41,76	42,42	0,66	b*1	31,74	31,88	0,14	0,74	
	L*2	55,94	55,75	-0,19	a*2	40,23	40,53	0,3	b*2	30,88	30,82	-0,06	0,36	
	L*3	54,4	56,34	1,94	a*3	42,6	41,46	-1,14	b*3	31,86	31,43	-0,43	2,29	
	L*Av	55,1	55,58	0,48	a*Av	41,53	41,47	-0,06	b*Av	31,49	31,38	-0,12	1,13	*1,02*
Inhibitor F	L*1	57,27	57,1	-0,17	a*1	39,26	39,86	0,6	b*1	30,87	31,43	0,56	0,84	
	L*2	58	58,43	0,43	a*2	38,35	38,28	-0,07	b*2	30,99	31	0,01	0,44	
	L*3	57,68	56,81	-0,87	a*3	39,34	40,2	0,86	b*3	31,64	31,4	-0,24	1,25	
	L*Av	57,65	57,45	-0,20	a*Av	38,98	39,45	0,46	b*Av	31,17	31,28	0,11	0,84	*0,41*
Inhibitor G	L*1	59,51	60,67	1,16	a*1	36,48	36,01	-0,47	b*1	28,09	29,26	1,17	1,71	
	L*2	60,49	60,04	-0,45	a*2	35	36,4	1,4	b*2	27,85	29,31	1,46	2,07	
	L*3	61,65	61,46	-0,19	a*3	34,15	35,79	1,64	b*3	27,78	29,92	2,14	2,70	
	L*Av	60,55	60,72	0,17	a*Av	35,21	36,07	0,86	b*Av	27,91	29,50	1,59	2,16	*0,50*
Inhibitor H	L*1	53,66	54,86	1,2	a*1	43,43	43,27	-0,16	b*1	30,85	31,18	0,33	1,25	
	L*2	53,54	54,89	1,35	a*2	43,12	42,85	-0,27	b*2	30,84	31	0,16	1,39	
	L*3	54,06	54,02	-0,04	a*3	43,49	42,8	-0,69	b*3	30,47	30,9	0,43	0,81	
	L*Av	53,75	54,59	0,84	a*Av	43,35	42,97	-0,37	b*Av	30,72	31,03	0,31	1,15	*0,30*
Inhibitor I	L*1	61,4	63,44	2,04	a*1	35,03	33,67	-1,36	b*1	31,73	30,28	-1,45	2,85	
	L*2	63,93	62,89	-1,04	a*2	32,75	34,73	1,98	b*2	31,04	31,55	0,51	2,29	
	L*3	62,94	63,98	1,04	a*3	33,48	32,74	-0,74	b*3	31,38	29,34	-2,04	2,41	
	L*Av	62,76	63,44	0,68	a*Av	33,75	33,71	-0,04	b*Av	31,38	30,39	-0,99	2,52	*0,29*

C.4.3 Colourimetric measurements of Brazilwood dyed samples exposed for 240h at 50°C

Treated samples	L*	before	After 240h	ΔL*	a*	before	after 240h	Δa*	b*	before	after 240h	Δb*	ΔE	Standard deviation
Blank	L*1	36,99	36,74	-0,25	a*1	47,22	47,04	-0,18	b*1	18,16	19,4	1,24	1,28	
	L*2	36,63	35,95	-0,68	a*2	47,49	46,77	-0,72	b*2	18,59	19,36	0,77	1,25	
	L*3	37,22	36,79	-0,43	a*3	48,36	46,73	-1,63	b*3	19,13	19,12	-0,01	1,69	
	L*Av	36,95	36,49	-0,45	a*Av	47,69	46,85	-0,84	b*Av	18,63	19,29	0,67	1,41	*0,24*
Inhibitor A	L*1	36,59	36,69	0,1	a*1	47,65	46,7	-0,95	b*1	18,86	19,64	0,78	1,23	
	L*2	36,14	30,09	-6,05	a*2	47,57	46,2	-1,37	b*2	18,98	16,63	-2,35	6,63	
	L*3	36,81	37,85	1,04	a*3	47,84	47,13	-0,71	b*3	19,24	19,64	0,4	1,32	
	L*Av	36,51	34,88	-1,64	a*Av	47,69	46,68	-1,01	b*Av	19,03	18,64	-0,39	3,06	*3,09*
Inhibitor B	L*1	35,8	35,39	-0,41	a*1	47,37	46,7	-0,67	b*1	18,73	19,23	0,5	0,93	
	L*2	36,87	35,88	-0,99	a*2	46,99	46,22	-0,77	b*2	17,88	18,88	1	1,60	
	L*3	35,91	34,99	-0,92	a*3	47,55	46,43	-1,12	b*3	18,54	19,15	0,61	1,57	
	L*Av	36,19	35,42	-0,77	a*Av	47,30	46,45	-0,85	b*Av	18,38	19,09	0,70	1,37	*0,38*
Inhibitor C	L*1	39,74	37,42	-2,32	a*1	41,97	45,68	3,71	b*1	13,35	18,35	5	6,64	
	L*2	39,45	37,03	-2,42	a*2	41,85	45,91	4,06	b*2	13,5	18,59	5,09	6,95	
	L*3	40,11	37,56	-2,55	a*3	42,54	45,25	2,71	b*3	13,36	18,04	4,68	5,98	
	L*Av	39,77	37,34	-2,43	a*Av	42,12	45,61	3,49	b*Av	13,40	18,33	4,92	6,52	*0,49*
Inhibitor D	L*1	35,27	34,62	-0,65	a*1	44,92	43,64	-1,28	b*1	16,99	17,25	0,26	1,46	
	L*2	35,49	35,57	0,08	a*2	45,24	43,86	-1,38	b*2	17,42	17,51	0,09	1,39	
	L*3	35,1	35,33	0,23	a*3	45,37	43,98	-1,39	b*3	17,46	17,59	0,13	1,41	
	L*Av	35,29	35,17	-0,11	a*Av	45,18	43,83	-1,35	b*Av	17,29	17,45	0,16	1,42	*0,04*

Treated samples	L*	before	After 240h	ΔL*	a*	before	after 240h	Δa*	b*	before	after 240h	Δb*	ΔE	Standard deviation
Inhibitor E	L*1	36,23	36,63	0,4	a*1	46,46	45,53	-0,93	b*1	18,73	19,12	0,39	1,08	
	L*2	37,34	36,02	-1,32	a*2	46,9	44,45	-2,45	b*2	18,76	18,32	-0,44	2,82	
	L*3	36,76	36,55	-0,21	a*3	47,5	46,02	-1,48	b*3	19,34	19,44	0,1	1,50	
	L*Av	36,78	36,40	-0,38	a*Av	46,95	45,33	-1,62	b*Av	18,94	18,96	0,02	1,80	*0,90*
Inhibitor F	L*1	36,56	35,65	-0,91	a*1	45,7	44,9	-0,8	b*1	17,73	18,7	0,97	1,55	
	L*2	36,05	36,04	-0,01	a*2	45,69	45,2	-0,49	b*2	17,6	18,53	0,93	1,05	
	L*3	36,22	35,89	-0,33	a*3	45,92	44,76	-1,16	b*3	17,92	18,36	0,44	1,28	
	L*Av	36,28	35,86	-0,42	a*Av	45,77	44,95	-0,82	b*Av	17,75	18,53	0,78	1,30	*0,25*
Inhibitor G	L*1	35,23	34,77	-0,46	a*1	45,68	44,1	-1,58	b*1	17,96	18,21	0,25	1,66	
	L*2	35,41	34,77	-0,64	a*2	45,41	44,9	-0,51	b*2	17,69	18,76	1,07	1,35	
	L*3	34,96	35,24	0,28	a*3	45,87	44,6	-1,27	b*3	18,07	18,5	0,43	1,37	
	L*Av	35,2	34,93	-0,27	a*Av	45,65	44,53	-1,12	b*Av	17,91	18,49	0,58	1,46	*0,18*
Inhibitor H	L*1	33,64	33	-0,64	a*1	45,05	43,31	-1,74	b*1	18,12	17,49	-0,63	1,96	
	L*2	33,66	33	-0,66	a*2	44,59	42,45	-2,14	b*2	17,88	17,07	-0,81	2,38	
	L*3	33,65	32,94	-0,71	a*3	45,33	42,07	-3,26	b*3	18,26	16,81	-1,45	3,64	
	L*Av	33,65	32,98	-0,67	a*Av	44,99	42,61	-2,38	b*Av	18,09	17,12	-0,96	2,66	*0,87*
Inhibitor I	L*1	36,01	35,76	-0,25	a*1	43,98	44,53	0,55	b*1	14,9	17,74	2,84	2,90	
	L*2	36,91	35,1	-1,81	a*2	44,42	44,84	0,42	b*2	14,89	18	3,11	3,62	
	L*3	36,77	35,87	-0,9	a*3	43,82	45,13	1,31	b*3	14,73	18,06	3,33	3,69	
	L*Av	36,56	35,58	-0,99	a*Av	44,07	44,83	0,76	b*Av	14,84	17,93	3,09	3,41	*0,44*

C.4.4 Colourimetric measurements of Brazilwood dyed samples exposed for 400h at 50°C

Treated samples	L*	before	after 400h	ΔL*	a*	before	after 400h	Δa*	b*	before	after 400h	Δb*	ΔE	Standard deviation
Blank	L*1	36,99	36,49	-0,5	a*1	47,22	46,99	-0,23	b*1	18,16	19,4	1,24	1,36	
	L*2	36,63	36,77	0,14	a*2	47,49	46,94	-0,55	b*2	18,59	19,39	0,8	0,98	
	L*3	37,22	36,89	-0,33	a*3	48,36	47,48	-0,88	b*3	19,13	19,61	0,48	1,06	
	L*Av	36,95	36,72	-0,23	a*Av	47,69	47,14	-0,55	b*Av	18,63	19,47	0,84	1,13	*0,20*
Inhibitor A	L*1	38,52	36,69	-1,83	a*1	47,65	48,79	1,14	b*1	18,86	20,87	2,01	2,95	
	L*2	39,04	36,65	-2,39	a*2	47,57	48,36	0,79	b*2	18,98	20,58	1,6	2,98	
	L*3	37,31	37,85	0,54	a*3	47,84	46,45	-1,39	b*3	19,24	19,2	-0,04	1,49	
	L*Av	38,29	37,06	-1,23	a*Av	47,69	47,87	0,18	b*Av	19,03	20,22	1,19	2,47	*0,85*
Inhibitor B	L*1	35,8	36,41	0,61	a*1	47,37	46,69	-0,68	b*1	18,73	19,24	0,51	1,05	
	L*2	36,87	36,5	-0,37	a*2	46,99	47,45	0,46	b*2	17,88	19,43	1,55	1,66	
	L*3	35,91	37,49	1,58	a*3	47,55	45,05	-2,5	b*3	18,54	18,17	-0,37	2,98	
	L*Av	36,19	36,80	0,61	a*Av	47,30	46,40	-0,91	b*Av	18,38	18,95	0,56	1,90	*0,99*
Inhibitor C	L*1	39,74	38,72	-1,02	a*1	41,97	46,65	4,68	b*1	13,35	19,03	5,68	7,43	
	L*2	39,45	37,72	-1,73	a*2	41,85	46,4	4,55	b*2	13,5	18,77	5,27	7,17	
	L*3	40,11	37,93	-2,18	a*3	42,54	46,29	3,75	b*3	13,36	18,57	5,21	6,78	
	L*Av	39,77	38,12	-1,64	a*Av	42,12	46,45	4,33	b*Av	13,40	18,79	5,39	7,13	*0,33*
Inhibitor D	L*1	35,27	36,55	1,28	a*1	44,92	44,92	0	b*1	16,99	17,8	0,81	1,51	
	L*2	35,49	35,88	0,39	a*2	45,24	44,29	-0,95	b*2	17,42	17,02	-0,4	1,10	
	L*3	35,1	36,61	1,51	a*3	45,37	45,29	-0,08	b*3	17,46	17,99	0,53	1,60	
	L*Av	35,29	36,35	1,06	a*Av	45,18	44,83	-0,34	b*Av	17,29	17,60	0,31	1,41	*0,27*

Treated samples	L*	before	after 400h	ΔL*	a*	before	after 400h	Δa*	b*	before	after 400h	Δb*	ΔE	Standard deviation
Inhibitor E	L*1	36,23	36,54	0,31	a*1	46,46	45,13	-1,33	b*1	18,73	18,65	-0,08	1,37	
	L*2	37,34	37,89	0,55	a*2	46,9	45,93	-0,97	b*2	18,76	18,87	0,11	1,12	
	L*3	36,76	36,04	-0,72	a*3	47,5	45,12	-2,38	b*3	19,34	18,61	-0,73	2,59	
	L*Av	36,78	36,82	0,05	a*Av	46,95	45,39	-1,56	b*Av	18,94	18,71	-0,23	1,69	*0,79*
Inhibitor F	L*1	36,56	36,27	-0,29	a*1	45,7	45,88	0,18	b*1	17,73	18,9	1,17	1,22	
	L*2	36,05	36,54	0,49	a*2	45,69	45,33	-0,36	b*2	17,6	18,67	1,07	1,23	
	L*3	36,22	36,4	0,18	a*3	45,92	45,84	-0,08	b*3	17,92	18,86	0,94	0,96	
	L*Av	36,28	36,40	0,13	a*Av	45,77	45,68	-0,09	b*Av	17,75	18,81	1,06	1,14	*0,15*
Inhibitor G	L*1	35,23	35,95	0,72	a*1	45,68	45,64	-0,04	b*1	17,96	18,91	0,95	1,19	
	L*2	35,41	36,27	0,86	a*2	45,41	45,33	-0,08	b*2	17,69	18,7	1,01	1,33	
	L*3	34,96	35,22	0,26	a*3	45,87	45,93	0,06	b*3	18,07	19,18	1,11	1,14	
	L*Av	35,2	35,81	0,61	a*Av	45,65	45,63	-0,02	b*Av	17,91	18,93	1,02	1,22	*0,10*
Inhibitor H	L*1	33,64	34,22	0,58	a*1	45,05	42,94	-2,11	b*1	18,12	17,05	-1,07	2,44	
	L*2	33,66	33,93	0,27	a*2	44,59	43,45	-1,14	b*2	17,88	17,39	-0,49	1,27	
	L*3	33,67	34,39	0,72	a*3	45,33	43,31	-2,02	b*3	18,26	17,32	-0,94	2,34	
	L*Av	33,66	34,18	0,52	a*Av	44,99	43,23	-1,76	b*Av	18,09	17,25	-0,83	2,02	*0,65*
Inhibitor I	L*1	36,01	35,57	-0,44	a*1	43,98	45,02	1,04	b*1	14,9	18,01	3,11	3,31	
	L*2	36,91	35,76	-1,15	a*2	44,42	45,66	1,24	b*2	14,89	18,43	3,54	3,92	
	L*3	36,77	35,93	-0,84	a*3	43,82	45,34	1,52	b*3	14,73	18,11	3,38	3,80	
	L*Av	36,56	35,75	-0,81	a*Av	44,07	45,34	1,27	b*Av	14,84	18,18	3,34	3,68	*0,33*

C.4.5 Colourimetric measurements of Safflower dyed samples exposed for 240h at 50°C

Treated samples	L*	before	after 240h	ΔL*	a*	before	after 240h	Δa*	b*	before	after 240h	Δb*	ΔE	Standard deviation
Blank	L*1	81,52	81,31	-0,21	a*1	29,51	28,25	-1,26	b*1	17,01	16,56	-0,45	1,35	
	L*2	81,34	81,75	0,41	a*2	29,78	27,85	-1,93	b*2	17,08	16,78	-0,3	2,00	
	L*3	81,26	81,01	-0,25	a*3	29,84	29,05	-0,79	b*3	17,11	17,29	0,18	0,85	
	L*Av	81,37	81,36	-0,02	a*Av	29,71	28,38	-1,33	b*Av	17,07	16,88	-0,19	1,40	*0,58*
Inhibitor A	L*1	79,37	80,45	1,08	a*1	32,02	27,86	-4,16	b*1	20,39	18,01	-2,38	4,91	
	L*2	79,24	80,31	1,07	a*2	32,35	29,53	-2,82	b*2	20,92	18,1	-2,82	4,13	
	L*3	80,1	79,97	-0,13	a*3	31,01	28,67	-2,34	b*3	20,88	18,7	-2,18	3,20	
	L*Av	79,57	80,24	0,67	a*Av	31,79	28,69	-3,11	b*Av	20,73	18,27	-2,46	4,08	*0,86*
Inhibitor B	L*1	80,15	78,994	-1,156	a*1	30,57	30,45	-0,12	b*1	19,45	18,58	-0,87	1,45	
	L*2	79,9	79,59	-0,31	a*2	31,07	30,03	-1,04	b*2	20,23	18,06	-2,17	2,43	
	L*3	79,86	78,31	-1,55	a*3	31,14	30,7	-0,44	b*3	19,98	18,96	-1,02	1,91	
	L*Av	79,97	78,96	-1,01	a*Av	30,93	30,39	-0,53	b*Av	19,89	18,53	-1,35	1,93	*0,49*
Inhibitor C	L*1	79,47	80,34	0,87	a*1	30,93	28,33	-2,6	b*1	22,39	20,56	-1,83	3,30	
	L*2	78,79	79,61	0,82	a*2	32,08	29,93	-2,15	b*2	20,97	21,07	0,1	2,30	
	L*3	79,52	79,76	0,24	a*3	30,91	29,5	-1,41	b*3	21,54	21,67	0,13	1,44	
	L*Av	79,26	79,90	0,64	a*Av	31,31	29,25	-2,05	b*Av	21,63	21,10	-0,53	2,35	*0,93*
Inhibitor D	L*1	80,67	79,53	-1,14	a*1	30,02	29,87	-0,15	b*1	18,33	17,65	-0,68	1,34	
	L*2	80,36	80,78	0,42	a*2	30,84	28,66	-2,18	b*2	19,93	18,86	-1,07	2,46	
	L*3	80,45	81,24	0,79	a*3	29,22	27,77	-1,45	b*3	18,95	18,94	-0,01	1,65	
	L*Av	80,49	80,52	0,02	a*Av	30,03	28,77	-1,26	b*Av	19,07	18,48	-0,59	1,82	*0,58*

Treated samples	L*	before	after 240h	ΔL*	a*	before	after 240h	Δa*	b*	before	after 240h	Δb*	ΔE	Standard deviation
Inhibitor E	L*1	78,55	79,66	1,11	a*1	31,8	30,33	-1,47	b*1	19,04	19,01	-0,03	1,84	
	L*2	79,19	79,82	0,63	a*2	31,53	29,6	-1,93	b*2	18,63	18,18	-0,45	2,08	
	L*3	78,62	79,2	0,58	a*3	33,06	30,43	-2,63	b*3	19,62	19,28	-0,34	2,71	
	L*Av	78,79	79,56	0,77	a*Av	32,13	30,12	-2,01	b*Av	19,10	18,82	-0,27	2,21	*0,45*
Inhibitor F	L*1	79,42	79,2	-0,22	a*1	31,51	30,13	-1,38	b*1	20,22	18,21	-2,01	2,45	
	L*2	79,68	79,11	-0,57	a*2	31,5	30,42	-1,08	b*2	19,78	19,85	0,07	1,22	
	L*3	79,88	80,1	0,22	a*3	31,25	29,31	-1,94	b*3	20,19	19,74	-0,45	2,00	
	L*Av	79,66	79,47	-0,19	a*Av	31,42	29,95	-1,47	b*Av	20,06	19,27	-0,80	1,89	*0,62*
Inhibitor G	L*1	80,24	80,56	0,32	a*1	30,86	28,57	-2,29	b*1	19,35	18,17	-1,18	2,60	
	L*2	79,63	79,7	0,07	a*2	32,02	29,11	-2,91	b*2	19,29	18,39	-0,9	3,05	
	L*3	80,57	80,43	-0,14	a*3	30,69	28,46	-2,23	b*3	18,49	17,99	-0,5	2,29	
	L*Av	80,15	80,23	0,08	a*Av	31,19	28,71	-2,48	b*Av	19,04	18,18	-0,86	2,64	*0,38*
Inhibitor H	L*1	79,08	78,31	-0,77	a*1	32,51	31,89	-0,62	b*1	19,8	20,32	0,52	1,12	
	L*2	78,74	78,72	-0,02	a*2	33,08	31,22	-1,86	b*2	19,58	20,8	1,22	2,22	
	L*3	78,58	78,84	0,26	a*3	33,4	31,63	-1,77	b*3	19,94	19,68	-0,26	1,81	
	L*Av	78,8	78,62	-0,18	a*Av	33,00	31,58	-1,42	b*Av	19,77	20,27	0,49	1,72	*0,56*
Inhibitor I	L*1	79,58	80,47	0,89	a*1	32,11	28,85	-3,26	b*1	20,55	18,48	-2,07	3,96	
	L*2	79,64	80,47	0,83	a*2	31,05	29,09	-1,96	b*2	20,31	18,9	-1,41	2,55	
	L*3	80,22	79,98	-0,24	a*3	30,59	28,94	-1,65	b*3	20,42	18,05	-2,37	2,90	
	L*Av	79,81	80,31	0,49	a*Av	31,25	28,96	-2,29	b*Av	20,43	18,48	-1,95	3,14	*0,73*

C.4.6 Colourimetric measurements of Safflower dyed samples exposed for 400h at 50°C

Treated samples	L*	before	after 400h	ΔL*	a*	before	after 400h	Δa*	b*	before	after 400h	Δb*	ΔE	Standard deviation
Blank	L*1	81,52	81,49	-0,03	a*1	29,51	27,4	-2,11	b*1	17,01	17,53	0,52	2,17	
	L*2	81,34	81,51	0,17	a*2	29,78	28,19	-1,59	b*2	17,08	17,32	0,24	1,62	
	L*3	81,26	81,61	0,35	a*3	29,84	27,67	-2,17	b*3	17,11	17,77	0,66	2,29	
	L*Av	81,37	81,54	0,16	a*Av	29,71	27,75	-1,96	b*Av	17,07	17,54	0,47	2,03	*0,36*
Inhibitor A	L*1	79,37	81,08	1,71	a*1	32,02	26,99	-5,03	b*1	20,39	19,7	-0,69	5,36	
	L*2	79,24	81,35	2,11	a*2	32,35	27,33	-5,02	b*2	20,92	18,93	-1,99	5,80	
	L*3	80,1	80,9	0,8	a*3	31,01	27,44	-3,57	b*3	20,88	20,01	-0,87	3,76	
	L*Av	79,57	81,11	1,54	a*Av	31,79	27,25	-4,54	b*Av	20,73	19,55	-1,18	4,97	*1,07*
Inhibitor B	L*1	80,15	80,56	0,41	a*1	30,57	28,32	-2,25	b*1	19,45	20,72	1,27	2,62	
	L*2	79,9	80,31	0,41	a*2	31,07	29,88	-1,19	b*2	20,23	20,18	-0,05	1,26	
	L*3	79,86	80,78	0,92	a*3	31,14	27,72	-3,42	b*3	19,98	19,8	-0,18	3,55	
	L*Av	79,97	80,55	0,58	a*Av	30,93	28,64	-2,29	b*Av	19,89	20,23	0,35	2,47	*1,15*
Inhibitor C	L*1	79,47	81,18	1,71	a*1	30,93	27,39	-3,54	b*1	22,39	21,48	-0,91	4,04	
	L*2	78,79	81,03	2,24	a*2	32,08	28,43	-3,65	b*2	20,97	21,35	0,38	4,30	
	L*3	79,52	79,76	0,24	a*3	30,91	29,24	-1,67	b*3	21,54	21,3	-0,24	1,70	
	L*Av	79,26	80,66	1,40	a*Av	31,31	28,35	-2,95	b*Av	21,63	21,38	-0,26	3,35	*1,43*
Inhibitor D	L*1	80,67	81,3	0,63	a*1	30,02	27,66	-2,36	b*1	18,33	20,52	2,19	3,28	
	L*2	80,36	80,37	0,01	a*2	30,84	28,96	-1,88	b*2	19,93	19,81	-0,12	1,88	
	L*3	80,45	81,13	0,68	a*3	29,22	27,92	-1,3	b*3	18,95	19,9	0,95	1,75	
	L*Av	80,49	80,93	0,44	a*Av	30,03	28,18	-1,85	b*Av	19,07	20,08	1,01	2,30	*0,85*

Treated samples	L*	before	after 400h	ΔL	a*	before	after 400h	Δa	b*	before	after 400h	Δb	ΔE	Standard deviation
Inhibitor E	L*1	78,55	79,76	1,21	a*1	31,8	29,14	-2,66	b*1	19,04	19,92	0,88	3,05	
	L*2	79,19	79,33	0,14	a*2	31,53	30,67	-0,86	b*2	18,63	20,22	1,59	1,81	
	L*3	78,62	79,37	0,75	a*3	33,06	30,38	-2,68	b*3	19,62	20,68	1,06	2,98	
	L*Av	78,79	79,49	0,70	a*Av	32,13	30,06	-2,07	b*Av	19,10	20,27	1,18	2,61	*0,69*
Inhibitor F	L*1	79,42	78,76	-0,66	a*1	31,51	28,27	-3,24	b*1	20,22	19,92	-0,3	3,32	
	L*2	79,68	74,99	-4,69	a*2	31,5	32,46	0,96	b*2	19,78	20,22	0,44	4,81	
	L*3	79,88	79,74	-0,14	a*3	31,25	28,99	-2,26	b*3	20,19	20,68	0,49	2,32	
	L*Av	79,66	77,83	-1,83	a*Av	31,42	29,91	-1,51	b*Av	20,06	20,27	0,21	3,48	*1,25*
Inhibitor G	L*1	80,24	81,43	1,19	a*1	30,86	27,23	-3,63	b*1	19,35	19,39	0,04	3,82	
	L*2	79,63	81,4	1,77	a*2	32,02	27,54	-4,48	b*2	19,29	18,78	-0,51	4,84	
	L*3	80,57	79,69	-0,88	a*3	30,69	30,15	-0,54	b*3	18,49	18,58	0,09	1,04	
	L*Av	80,15	80,84	0,69	a*Av	31,19	28,31	-2,88	b*Av	19,04	18,92	-0,13	3,23	*1,97*
Inhibitor H	L*1	79,08	78,81	-0,27	a*1	32,51	31,16	-1,35	b*1	19,8	21,46	1,66	2,16	
	L*2	78,74	79	0,26	a*2	33,08	31,48	-1,6	b*2	19,58	21,41	1,83	2,44	
	L*3	78,58	78,91	0,33	a*3	33,4	31,46	-1,94	b*3	19,94	21,73	1,79	2,66	
	L*Av	78,80	78,91	0,11	a*Av	33,00	31,37	-1,63	b*Av	19,77	21,53	1,76	2,42	*0,25*
Inhibitor I	L*1	79,58	80,69	1,11	a*1	32,11	28,6	-3,51	b*1	20,55	18,65	-1,9	4,14	
	L*2	79,64	81,24	1,6	a*2	31,05	27,74	-3,31	b*2	20,31	19,45	-0,86	3,78	
	L*3	80,22	80,25	0,03	a*3	30,59	29,26	-1,33	b*3	20,42	18,87	-1,55	2,04	
	L*Av	79,81	80,73	0,91	a*Av	31,25	28,53	-2,72	b*Av	20,43	18,99	-1,44	3,32	*1,12*

C.4.7 Colourimetric measurements of Cochineal dyed samples exposed for 240h at 50°C

Treated samples	L*	before	after	ΔL*	a*	before	after	Δa*	b*	before	after	Δb*	ΔE	Standard deviation
Blank	L*1	30,61	30,24	-0,37	a*1	45,28	44,85	-0,43	b*1	11,16	10,47	-0,69	0,89	
	L*2	30,07	30,34	0,27	a*2	46,2	44,72	-1,48	b*2	11,56	10,45	-1,11	1,87	
	L*3	29,98	30,23	0,25	a*3	45,64	44,79	-0,85	b*3	11,27	10,51	-0,76	1,17	
	L*Av	30,22	30,27	0,05	a*Av	45,71	44,79	-0,92	b*Av	11,33	10,48	-0,85	1,31	*0,50*
Inhibitor A	L*1	29,88	30,85	0,97	a*1	41,54	44,05	2,51	b*1	9,4	9,87	0,47	2,73	
	L*2	29,52	30,46	0,94	a*2	42,76	44,45	1,69	b*2	9,73	10,1	0,37	1,97	
	L*3	29,58	30,22	0,64	a*3	42,74	44,11	1,37	b*3	9,82	9,87	0,05	1,51	
	L*Av	29,66	30,51	0,85	a*Av	42,35	44,20	1,86	b*Av	9,65	9,95	0,30	2,07	*0,62*
Inhibitor B	L*1	31,04	29,24	-1,8	a*1	45,07	42,21	-2,86	b*1	10	9,42	-0,58	3,43	
	L*2	31,12	29,45	-1,67	a*2	44,72	42,1	-2,62	b*2	9,7	9,47	-0,23	3,12	
	L*3	30,29	30,53	0,24	a*3	44,47	42,98	-1,49	b*3	9,39	9,56	0,17	1,52	
	L*Av	30,82	29,74	-1,08	a*Av	44,75	42,43	-2,32	b*Av	9,70	9,48	-0,21	2,69	*1,02*
Inhibitor C	L*1	32,23	31,76	-0,47	a*1	42,21	41,9	-0,31	b*1	8,69	8,86	0,17	0,59	
	L*2	33,61	32,17	-1,44	a*2	41,45	41,8	0,35	b*2	7,85	8,97	1,12	1,86	
	L*3	33,62	32,62	-1	a*3	41,28	42,56	1,28	b*3	7,86	9,07	1,21	2,03	
	L*Av	33,15	32,18	-0,97	a*Av	41,65	42,09	0,44	b*Av	8,13	8,97	0,83	1,49	*0,79*
Inhibitor D	L*1	30,1	30,4	0,3	a*1	44	43,96	-0,04	b*1	10,95	10,68	-0,27	0,41	
	L*2	30,05	31,26	1,21	a*2	44,46	44,35	-0,11	b*2	11,11	10,15	-0,96	1,55	
	L*3	30,03	31,61	1,58	a*3	45,02	44,39	-0,63	b*3	11,35	10,25	-1,1	2,03	
	L*Av	30,06	31,09	1,03	a*Av	44,49	44,23	-0,26	b*Av	11,14	10,36	-0,78	1,33	*0,83*

Treated samples	L*	before	after	ΔL*	a*	before	after	Δa*	b*	before	after	Δb*	ΔE	Standard deviation
Inhibitor E	L*1	30,35	28,81	-1,54	a*1	42,54	41,22	-1,32	b*1	10,03	9,91	-0,12	2,03	
	L*2	29,29	29,51	0,22	a*2	40,5	42,12	1,62	b*2	9,67	10,09	0,42	1,69	
	L*3	29,11	29,02	-0,09	a*3	41,28	41,02	-0,26	b*3	9,94	9,76	-0,18	0,33	
	L*Av	29,58	29,11	-0,47	a*Av	41,44	41,45	0,01	b*Av	9,88	9,92	0,04	1,35	*0,90*
Inhibitor F	L*1	28,2	27,12	-1,08	a*1	42,94	41,94	-1	b*1	10,82	10,65	-0,17	1,48	
	L*2	27,92	27,42	-0,5	a*2	42,33	42,32	-0,01	b*2	10,69	10,75	0,06	0,50	
	L*3	27,54	27,93	0,39	a*3	42,4	41,85	-0,55	b*3	10,88	10,1	-0,78	1,03	
	L*Av	27,89	27,49	-0,40	a*Av	42,56	42,04	-0,52	b*Av	10,80	10,50	-0,30	1,01	*0,49*
Inhibitor G	L*1	28,64	29,51	0,87	a*1	42,19	43,42	1,23	b*1	9,75	10,17	0,42	1,56	
	L*2	29,01	29,98	0,97	a*2	43,15	44,3	1,15	b*2	10,29	10,07	-0,22	1,52	
	L*3	29,46	30,55	1,09	a*3	43,27	44,14	0,87	b*3	10,03	9,92	-0,11	1,40	
	L*Av	29,04	30,01	0,98	a*Av	42,87	43,95	1,08	b*Av	10,02	10,05	0,03	1,49	*0,09*
Inhibitor H	L*1	29,74	29,49	-0,25	a*1	41,95	42,02	0,07	b*1	10,23	9,13	-1,1	1,13	
	L*2	29,45	29,31	-0,14	a*2	42,38	41,91	-0,47	b*2	9,9	9,04	-0,86	0,99	
	L*3	30,23	29,25	-0,98	a*3	41,67	41,07	-0,6	b*3	9,42	9,05	-0,37	1,21	
	L*Av	29,81	29,35	-0,46	a*Av	42,00	41,67	-0,33	b*Av	9,85	9,07	-0,78	1,11	*0,11*
Inhibitor I	L*1	30,63	29,89	-0,74	a*1	45,67	44,74	-0,93	b*1	9,99	10,66	0,67	1,36	
	L*2	30,5	30,25	-0,25	a*2	43,88	44,82	0,94	b*2	9,25	10,46	1,21	1,55	
	L*3	31,04	28,12	-2,92	a*3	45,22	46,89	1,67	b*3	10,01	12,34	2,33	4,09	
	L*Av	30,72	29,42	-1,30	a*Av	44,92	45,48	0,56	b*Av	9,75	11,15	1,40	2,34	*1,52*

C.4.8 Colourimetric measurements of Cochineal dyed samples exposed for 400h at 50°C

Treated samples	L*	before	After 400h	ΔL*	a*	before	After 400h	Δa*	b*	before	After 400h	Δb*	ΔE	Standard deviation
Blank	L*1	30,61	30,46	-0,15	a*1	45,28	44,99	-0,29	b*1	11,16	11,48	0,32	0,46	
	L*2	30,07	30,44	0,37	a*2	46,2	44,77	-1,43	b*2	11,56	11,36	-0,2	1,49	
	L*3	29,98	30,99	1,01	a*3	45,64	44,79	-0,85	b*3	11,27	11,3	0,03	1,32	
	L*Av	30,22	30,63	0,41	a*Av	45,71	44,85	-0,86	b*Av	11,33	11,38	0,05	1,09	*0,55*
Inhibitor A	L*1	29,88	31,16	1,28	a*1	41,54	44,59	3,05	b*1	9,4	10,78	1,38	3,58	
	L*2	29,52	31,43	1,91	a*2	42,76	44,12	1,36	b*2	9,73	10,87	1,14	2,61	
	L*3	29,58	30,8	1,22	a*3	42,74	43,84	1,1	b*3	9,82	10,76	0,94	1,89	
	L*Av	29,66	31,13	1,47	a*Av	42,35	44,18	1,84	b*Av	9,65	10,80	1,15	2,69	*0,85*
Inhibitor B	L*1	31,04	30,77	-0,27	a*1	45,07	43,69	-1,38	b*1	10	10,21	0,21	1,42	
	L*2	31,12	31,44	0,32	a*2	44,72	43,53	-1,19	b*2	9,7	9,94	0,24	1,26	
	L*3	30,29	31,26	0,97	a*3	44,47	42,27	-2,2	b*3	9,39	9,59	0,2	2,41	
	L*Av	30,82	31,16	0,34	a*Av	44,75	43,16	-1,59	b*Av	9,70	9,91	0,22	1,70	*0,63*
Inhibitor C	L*1	32,23	32,77	0,54	a*1	42,21	42,95	0,74	b*1	8,69	10,12	1,43	1,70	
	L*2	33,61	32,81	-0,8	a*2	41,45	43,11	1,66	b*2	7,85	10	2,15	2,83	
	L*3	33,62	32,63	-0,99	a*3	41,28	42,86	1,58	b*3	7,86	9,79	1,93	2,68	
	L*Av	33,15	32,74	-0,42	a*Av	41,65	42,97	1,33	b*Av	8,13	9,97	1,84	2,40	*0,62*
Inhibitor D	L*1	30,1	32,23	2,13	a*1	44	45,25	1,25	b*1	10,95	11,2	0,25	2,48	
	L*2	30,05	31,83	1,78	a*2	44,46	45,34	0,88	b*2	11,11	10,95	-0,16	1,99	
	L*3	30,03	31,41	1,38	a*3	45,02	43,79	-1,23	b*3	11,35	10,5	-0,85	2,03	
	L*Av	30,06	31,82	1,76	a*Av	44,49	44,79	0,30	b*Av	11,14	10,88	-0,25	2,17	*0,27*

Treated samples	L*	before	After 400h	ΔL*	a*	before	After 400h	Δa*	b*	before	After 400h	Δb*	ΔE	Standard deviation
Inhibitor E	L*1	30,35	29,96	-0,39	a*1	42,54	41,67	-0,87	b*1	10,03	10,48	0,45	1,05	
	L*2	29,29	30,12	0,83	a*2	40,5	41,99	1,49	b*2	9,67	10,11	0,44	1,76	
	L*3	29,11	29,93	0,82	a*3	41,28	42,68	1,4	b*3	9,94	10,54	0,6	1,73	
	L*Av	29,58	30,00	0,42	a*Av	41,44	42,11	0,67	b*Av	9,88	10,38	0,50	1,52	*0,40*
Inhibitor F	L*1	28,2	28,77	0,57	a*1	42,94	42,9	-0,04	b*1	10,82	11,4	0,58	0,81	
	L*2	27,92	28,82	0,9	a*2	42,33	43,54	1,21	b*2	10,69	10,89	0,2	1,52	
	L*3	27,54	28,41	0,87	a*3	42,4	43,86	1,46	b*3	10,88	11,58	0,7	1,84	
	L*Av	27,89	28,67	0,78	a*Av	42,56	43,43	0,88	b*Av	10,80	11,29	0,49	1,39	*0,52*
Inhibitor G	L*1	28,64	30,21	1,57	a*1	42,19	42,4	0,21	b*1	9,75	10,15	0,4	1,63	
	L*2	29,01	29,69	0,68	a*2	43,15	44,65	1,5	b*2	10,29	11,68	1,39	2,16	
	L*3	29,46	30,56	1,1	a*3	43,27	44,45	1,18	b*3	10,03	11,3	1,27	2,05	
	L*Av	29,04	30,15	1,12	a*Av	42,87	43,83	0,96	b*Av	10,02	11,04	1,02	1,95	*0,28*
Inhibitor H	L*1	29,74	30,15	0,41	a*1	41,95	42,41	0,46	b*1	10,23	9,76	-0,47	0,77	
	L*2	29,45	29,09	-0,36	a*2	42,38	41,95	-0,43	b*2	9,9	9,75	-0,15	0,58	
	L*3	30,23	29,7	-0,53	a*3	41,67	42,61	0,94	b*3	9,42	10,67	1,25	1,65	
	L*Av	29,81	29,65	-0,16	a*Av	42,00	42,32	0,32	b*Av	9,85	10,06	0,21	1,00	*0,57*
Inhibitor I	L*1	30,63	31,04	0,41	a*1	45,67	45,6	-0,07	b*1	9,99	11,09	1,1	1,18	
	L*2	30,5	30,32	-0,18	a*2	43,88	44,6	0,72	b*2	9,25	11,06	1,81	1,96	
	L*3	31,04	29,45	-1,59	a*3	45,22	46,05	0,83	b*3	10,01	12,35	2,34	2,95	
	L*Av	30,72	30,27	-0,45	a*Av	44,92	45,42	0,49	b*Av	9,75	11,5	1,75	2,03	*0,89*

C.4.9 Colourimetric measurements of Combination 1 dyed samples exposed for 260h at 50°C

Treated samples	L*	before	After 260h	ΔL*	a*	before	After 260h	Δa*	b*	before	After 260h	Δb*	ΔE	Standard deviation
Blank	L*1	57,09	56,45	-0,64	a*1	36,09	36,83	0,74	b*1	30,84	31,19	0,35	1,04	
	L*2	57,88	57,53	-0,35	a*2	36,46	36,3	-0,16	b*2	31,21	31,37	0,16	0,42	
	L*3	57,16	57,2	0,04	a*3	35,9	36,58	0,68	b*3	30,67	31,16	0,49	0,84	
	L*Av	57,38	57,06	-0,32	a*Av	36,15	36,57	0,42	b*Av	30,91	31,24	0,33	0,76	*0,32*
Inhibitor A	L*1	53,39	55,08	1,69	a*1	38,24	37,53	-0,71	b*1	30,83	30,99	0,16	1,84	
	L*2	53,64	54,93	1,29	a*2	37,94	37,48	-0,46	b*2	30,88	30,9	0,02	1,37	
	L*3	52,77	54,07	1,3	a*3	38,15	38,15	0	b*3	30,76	30,95	0,19	1,31	
	L*Av	53,27	54,69	1,43	a*Av	38,11	37,72	-0,39	b*Av	30,82	30,95	0,12	1,51	*0,29*
Inhibitor B	L*1	57,45	56,44	-1,01	a*1	35,21	36,73	1,52	b*1	30,38	32,23	1,85	2,60	
	L*2	58,13	55,96	-2,17	a*2	34,84	37,21	2,37	b*2	30,95	32,71	1,76	3,66	
	L*3	57,58	55,32	-2,26	a*3	35,14	37,72	2,58	b*3	30,59	32,25	1,66	3,81	
	L*Av	57,72	55,91	-1,81	a*Av	35,06	37,22	2,16	b*Av	30,64	32,40	1,76	3,36	*0,66*
Inhibitor C	L*1	55,46	54,26	-1,2	a*1	37,19	37,72	0,53	b*1	27,41	28,22	0,81	1,54	
	L*2	55,07	55,02	-0,05	a*2	37,2	37,2	0	b*2	27,23	28,46	1,23	1,23	
	L*3	55,06	55,64	0,58	a*3	37,53	35,99	-1,54	b*3	27,85	27,58	-0,27	1,67	
	L*Av	55,20	54,97	-0,22	a*Av	37,31	36,97	-0,34	b*Av	27,50	28,09	0,59	1,48	*0,22*
Inhibitor D	L*1	53,51	53,21	-0,3	a*1	37,01	36,84	-0,17	b*1	31,16	31,4	0,24	0,42	
	L*2	53,69	53,72	0,03	a*2	37,56	36,75	-0,81	b*2	31,48	30,62	-0,86	1,18	
	L*3	53,39	52,8	-0,59	a*3	37,31	37,39	0,08	b*3	31,51	31,02	-0,49	0,77	
	L*Av	53,53	53,24	-0,29	a*Av	37,29	36,99	-0,30	b*Av	31,38	31,01	-0,37	0,79	*0,38*

Treated samples	L*	before	After 260h	ΔL*	a*	before	After 260h	Δa*	b*	before	After 260h	Δb*	ΔE	Standard deviation
Inhibitor E	L*1	56,13	57,34	1,21	a*1	38,26	37,35	-0,91	b*1	32,12	31,86	-0,26	1,54	
	L*2	57,17	56,35	-0,82	a*2	37,36	37,44	0,08	b*2	31,95	31,85	-0,1	0,83	
	L*3	56,85	57,33	0,48	a*3	37,4	37,81	0,41	b*3	31,74	32,05	0,31	0,70	
	L*Av	56,72	57,01	0,29	a*Av	37,67	37,53	-0,14	b*Av	31,94	31,92	-0,02	1,02	*0,45*
Inhibitor F	L*1	56,94	56,77	-0,17	a*1	36,71	36,87	0,16	b*1	32,38	33,1	0,72	0,76	
	L*2	55,08	57,33	2,25	a*2	31,23	36,32	5,09	b*2	31,23	32,95	1,72	5,82	
	L*3	56,22	54,31	-1,91	a*3	32,54	38,61	6,07	b*3	32,54	32,19	-0,35	6,37	
	L*Av	56,08	56,14	0,06	a*Av	33,49	37,27	3,77	b*Av	32,05	32,75	0,70	4,32	*3,10*
Inhibitor G	L*1	55,17	55,04	-0,13	a*1	38,76	38,31	-0,45	b*1	31,52	31,29	-0,23	0,52	
	L*2	55,07	54,17	-0,9	a*2	38,59	37,91	-0,68	b*2	31,76	30,65	-1,11	1,58	
	L*3	56,21	54,54	-1,67	a*3	38,05	37,96	-0,09	b*3	31,35	30,66	-0,69	1,81	
	L*Av	55,48	54,58	-0,90	a*Av	38,47	38,06	-0,41	b*Av	31,54	30,87	-0,68	1,30	*0,69*
Inhibitor H	L*1	54,56	55,77	1,21	a*1	39,02	37,17	-1,85	b*1	31,93	30,38	-1,55	2,70	
	L*2	54,83	53,79	-1,04	a*2	38,5	37,86	-0,64	b*2	31,84	30,1	-1,74	2,13	
	L*3	55,08	55,31	0,23	a*3	37,57	37,71	0,14	b*3	30,77	30,45	-0,32	0,42	
	L*Av	54,82	54,96	0,13	a*Av	38,36	37,58	-0,78	b*Av	31,51	30,31	-1,20	1,75	*1,19*
Inhibitor I	L*1	57,62	55,45	-2,17	a*1	34,21	36,11	1,9	b*1	29,29	29,86	0,57	2,94	
	L*2	56,76	55,16	-1,6	a*2	36,06	36,51	0,45	b*2	29,85	29,19	-0,66	1,79	
	L*3	55,9	57,18	1,28	a*3	36,5	35,22	-1,28	b*3	30,17	30,32	0,15	1,82	
	L*Av	56,76	55,93	-0,83	a*Av	35,59	35,95	0,36	b*Av	29,77	29,79	0,02	2,18	*0,66*

C.4.10 Colourimetric measurements of Combination 1 dyed samples exposed for 400h at 50°C

Treated samples	L*	before	after	ΔL*	a*	before	after	Δa*	b*	before	after	Δb*	ΔE	Standard deviation
Blank	L*1	57,09	57,05	-0,04	a*1	36,09	36,47	0,38	b*1	30,84	31,5	0,66	0,76	
	L*2	57,88	58,46	0,58	a*2	36,46	35,89	-0,57	b*2	31,21	31,59	0,38	0,90	
	L*3	57,16	57,52	0,36	a*3	35,9	36,37	0,47	b*3	30,67	31,81	1,14	1,28	
	L*Av	57,38	57,68	0,30	a*Av	36,15	36,24	0,09	b*Av	30,91	31,63	0,73	0,98	0,27
Inhibitor A	L*1	53,39	55,46	2,07	a*1	38,24	37,76	-0,48	b*1	30,83	31,84	1,01	2,35	
	L*2	53,64	56,58	2,94	a*2	37,94	36,47	-1,47	b*2	30,88	31,42	0,54	3,33	
	L*3	52,77	55,84	3,07	a*3	38,15	37,99	-0,16	b*3	30,76	31,65	0,89	3,20	
	L*Av	53,27	55,96	2,69	a*Av	38,11	37,41	-0,70	b*Av	30,82	31,64	0,81	2,96	0,53
Inhibitor B	L*1	57,45	57,82	0,37	a*1	35,21	35,04	-0,17	b*1	30,38	31,89	1,51	1,56	
	L*2	58,13	57,95	-0,18	a*2	34,84	34,82	-0,02	b*2	30,95	30,97	0,02	0,18	
	L*3	57,58	56,94	-0,64	a*3	35,14	34,89	-0,25	b*3	30,59	31,61	1,02	1,23	
	L*Av	57,72	57,57	-0,15	a*Av	35,06	34,92	-0,15	b*Av	30,64	31,49	0,85	0,99	0,72
Inhibitor C	L*1	55,46	55,81	0,35	a*1	37,19	37,23	0,04	b*1	27,41	28,7	1,29	1,34	
	L*2	55,07	55,48	0,41	a*2	37,2	36,85	-0,35	b*2	27,23	29,1	1,87	1,95	
	L*3	55,06	56,26	1,2	a*3	37,53	37,06	-0,47	b*3	27,85	28,88	1,03	1,65	
	L*Av	55,20	55,85	0,65	a*Av	37,31	37,05	-0,26	b*Av	27,50	28,89	1,40	1,64	0,30
Inhibitor D	L*1	53,51	54,09	0,58	a*1	37,01	36,67	-0,34	b*1	31,16	31,26	0,1	0,68	
	L*2	53,69	54	0,31	a*2	37,56	37,45	-0,11	b*2	31,48	31,52	0,04	0,33	
	L*3	53,39	54,66	1,27	a*3	37,31	36,37	-0,94	b*3	31,51	31,05	-0,46	1,65	
	L*Av	53,53	54,25	0,72	a*Av	37,29	36,83	-0,46	b*Av	31,38	31,28	-0,11	0,89	0,68

Treated samples	L*	before	after	ΔL*	a*	before	after	Δa*	b*	before	after	Δb*	ΔE	Standard deviation
Inhibitor E	L*1	56,13	57,72	1,59	a*1	38,26	37,06	-1,2	b*1	32,12	32,29	0,17	2,00	
	L*2	57,17	57,09	-0,08	a*2	37,36	37,98	0,62	b*2	31,95	32,35	0,4	0,74	
	L*3	56,85	58,26	1,41	a*3	37,4	36,47	-0,93	b*3	31,74	32,11	0,37	1,73	
	L*Av	56,72	57,69	0,97	a*Av	37,67	37,17	-0,50	b*Av	31,94	32,25	0,31	1,49	0,66
Inhibitor F	L*1	56,94	56,7	-0,24	a*1	36,71	36,97	0,26	b*1	32,38	32,75	0,37	0,51	
	L*2	55,08	56,19	1,11	a*2	31,23	36,6	5,37	b*2	31,23	32,68	1,45	5,67	
	L*3	56,22	57,02	0,8	a*3	32,54	37,75	5,21	b*3	32,54	33,09	0,55	5,30	
	L*Av	56,08	56,64	0,56	a*Av	33,49	37,11	3,61	b*Av	32,05	32,84	0,79	3,83	2,88
Inhibitor G	L*1	55,17	54,75	-0,42	a*1	38,76	37,97	-0,79	b*1	31,52	31,11	-0,41	0,98	
	L*2	55,07	55,79	0,72	a*2	38,59	37,57	-1,02	b*2	31,76	30,29	-1,47	1,93	
	L*3	56,21	55,44	-0,77	a*3	38,05	38,44	0,39	b*3	31,35	31,27	-0,08	0,87	
	L*Av	55,48	55,33	-0,16	a*Av	38,47	37,99	-0,47	b*Av	31,54	30,89	-0,65	1,26	0,58
Inhibitor H	L*1	54,56	54,98	0,42	a*1	39,02	36,87	-2,15	b*1	31,93	29,94	-1,99	2,96	
	L*2	54,83	56,73	1,9	a*2	38,5	36,59	-1,91	b*2	31,84	30,97	-0,87	2,83	
	L*3	55,08	55,78	0,7	a*3	37,57	36,93	-0,64	b*3	30,77	30,41	-0,36	1,01	
	L*Av	54,82	55,83	1,01	a*Av	38,36	36,80	-1,57	b*Av	31,51	30,44	-1,07	2,27	1,09
Inhibitor I	L*1	57,62	56,71	-0,91	a*1	34,21	35,35	1,14	b*1	29,29	30,08	0,79	1,66	
	L*2	56,76	56,16	-0,6	a*2	36,06	36,85	0,79	b*2	29,85	30,77	0,92	1,35	
	L*3	55,9	55,1	-0,8	a*3	36,5	37,26	0,76	b*3	30,17	30,41	0,24	1,13	
	L*Av	56,76	55,99	-0,77	a*Av	35,59	36,49	0,90	b*Av	29,77	30,42	0,65	1,38	0,27

C.4.11 Colourimetric measurements of Combination 2 dyed samples exposed for 260h at 50°C

Treated samples	L*	before	After 260h	ΔL	a*	before	After 260h	Δa	b*	before	After 260h	Δb	ΔE	Standard deviation
Blank	L*1	58,02	55,17	-2,85	a*1	37,14	38,34	1,2	b*1	32,34	31,89	-0,45	3,12	
	L*2	56,13	54,95	-1,18	a*2	37,94	37,9	-0,04	b*2	32,2	31,39	-0,81	1,43	
	L*3	56,84	55,27	-1,57	a*3	36,91	37,57	0,66	b*3	32,13	31,87	-0,26	1,72	
	L*Av	57,00	55,13	-1,87	a*Av	37,33	37,94	0,61	b*Av	32,22	31,72	-0,51	2,09	*0,91*
Inhibitor A	L*1	58,04	59,28	1,24	a*1	31,81	30,53	-1,28	b*1	30,89	30,68	-0,21	1,79	
	L*2	58,39	59,08	0,69	a*2	30,22	31	0,78	b*2	29,96	30,72	0,76	1,29	
	L*3	58,17	59,75	1,58	a*3	30,46	30,61	0,15	b*3	29,72	30,57	0,85	1,80	
	L*Av	58,20	59,37	1,17	a*Av	30,83	30,71	-0,12	b*Av	30,19	30,66	0,47	1,63	*0,29*
Inhibitor B	L*1	58,97	56,89	-2,08	a*1	30,56	31,84	1,28	b*1	29,9	31,37	1,47	2,85	
	L*2	57,96	56,66	-1,3	a*2	31,03	30,92	-0,11	b*2	30,35	30,14	-0,21	1,32	
	L*3	58,45	56,96	-1,49	a*3	31,01	32,15	1,14	b*3	29,94	31,49	1,55	2,43	
	L*Av	58,46	56,84	-1,62	a*Av	30,87	31,64	0,77	b*Av	30,06	31,00	0,94	2,20	*0,79*
Inhibitor C	L*1	54,8	54,29	-0,51	a*1	33,39	27,09	-6,3	b*1	27,01	27,09	0,08	6,32	
	L*2	54,25	53,4	-0,85	a*2	33,89	26,92	-6,97	b*2	27,05	26,92	-0,13	7,02	
	L*3	55,52	55,41	-0,11	a*3	33,44	27,61	-5,83	b*3	26,95	27,61	0,66	5,87	
	L*Av	54,86	54,37	-0,49	a*Av	33,57	27,21	-6,37	b*Av	27,00	27,21	0,20	6,40	*0,58*
Inhibitor D	L*1	57,05	56,22	-0,83	a*1	31,74	31,89	0,15	b*1	30,89	29,34	-1,55	1,76	
	L*2	56,79	55,69	-1,1	a*2	31,24	31,62	0,38	b*2	29,85	29,36	-0,49	1,26	
	L*3	57,4	57,12	-0,28	a*3	31,19	30,77	-0,42	b*3	30,37	29,05	-1,32	1,41	
	L*Av	57,08	56,34	-0,74	a*Av	31,39	31,43	0,04	b*Av	30,37	29,25	-1,12	1,48	*0,26*

Treated samples	L*	before	After 260h	ΔL	a*	before	After 260h	Δa	b*	before	After 260h	Δb	ΔE	Standard deviation
Inhibitor E	L*1	57,41	57,7	0,29	a*1	34,07	33,56	-0,51	b*1	30,65	30,5	-0,15	0,61	
	L*2	58,3	56,35	-1,95	a*2	32,74	35,4	2,66	b*2	30,82	32,03	1,21	3,51	
	L*3	57,07	58,79	1,72	a*3	34,51	32,86	-1,65	b*3	31,13	30,6	-0,53	2,44	
	L*Av	57,59	57,61	0,02	a*Av	33,77	33,94	0,17	b*Av	30,87	31,04	0,18	2,19	*1,47*
Inhibitor F	L*1	59,27	58,53	-0,74	a*1	34,66	34,48	-0,18	b*1	32,81	32,36	-0,45	0,88	
	L*2	58,26	58,68	0,42	a*2	34,67	34,54	-0,13	b*2	32,96	31,65	-1,31	1,38	
	L*3	58,5	58,32	-0,18	a*3	34,91	34,47	-0,44	b*3	32,33	31,91	-0,42	0,63	
	L*Av	58,68	58,51	-0,17	a*Av	34,75	34,50	-0,25	b*Av	32,70	31,97	-0,73	0,97	*0,38*
Inhibitor G	L*1	59,26	58,52	-0,74	a*1	31,91	32,41	0,5	b*1	32,55	32,02	-0,53	1,04	
	L*2	59,79	58,9	-0,89	a*2	31,21	32,46	1,25	b*2	31,93	32,21	0,28	1,56	
	L*3	57,94	57,63	-0,31	a*3	32,23	32,79	0,56	b*3	32,04	31,48	-0,56	0,85	
	L*Av	59,00	58,35	-0,65	a*Av	31,78	32,55	0,77	b*Av	32,17	31,90	-0,27	1,15	*0,37*
Inhibitor H	L*1	58,71	58,13	-0,58	a*1	31,28	31,98	0,7	b*1	31,4	31,3	-0,1	0,91	
	L*2	58,49	60,53	2,04	a*2	31,8	28,92	-2,88	b*2	31,23	31,21	-0,02	3,53	
	L*3	61,01	57,9	-3,11	a*3	28,89	32	3,11	b*3	31,64	30,31	-1,33	4,59	
	L*Av	59,40	58,85	-0,55	a*Av	30,66	30,97	0,31	b*Av	31,42	30,94	-0,48	3,01	*1,89*
Inhibitor I	L*1	59,14	58,87	-0,27	a*1	29,36	30,08	0,72	b*1	29,12	28,87	-0,25	0,81	
	L*2	59,74	57,01	-2,73	a*2	28,85	31,44	2,59	b*2	28,17	30,18	2,01	4,27	
	L*3	58,37	59,03	0,66	a*3	30,83	30,1	-0,73	b*3	29,56	29,54	-0,02	0,98	
	L*Av	59,08	58,30	-0,78	a*Av	29,68	30,54	0,86	b*Av	28,95	29,53	0,58	2,02	*1,95*

C.4.12 Colourimetrric measurements of Combination 2 dyed samples exposed for 400h at 50°C

Treated samples	L*	before	After 400h	ΔL*	a*	before	After 400h	Δa*	b*	before	After 400h	Δb*	ΔE	Standard deviation
Blank	L*1	58,02	56,8	-1,22	a*1	37,14	36,89	-0,25	b*1	32,34	32,44	0,1	1,25	
	L*2	56,13	56,66	0,53	a*2	37,94	37,76	-0,18	b*2	32,2	32,42	0,22	0,60	
	L*3	56,84	56,1	-0,74	a*3	36,91	37,31	0,4	b*3	32,13	31,42	-0,71	1,10	
	L*Av	57,00	56,52	-0,48	a*Av	37,33	37,32	-0,01	b*Av	32,22	32,09	-0,13	0,98	*0,34*
Inhibitor A	L*1	58,04	59,88	1,84	a*1	31,81	30,44	-1,37	b*1	30,89	30,58	-0,31	2,31	
	L*2	58,39	59,23	0,84	a*2	30,22	30,86	0,64	b*2	29,96	30,61	0,65	1,24	
	L*3	58,17	55,81	-2,36	a*3	30,46	29,65	-0,81	b*3	29,72	28,86	-0,86	2,64	
	L*Av	58,20	58,31	0,11	a*Av	30,83	30,32	-0,51	b*Av	30,19	30,02	-0,17	2,06	*0,73*
Inhibitor B	L*1	58,97	58,43	-0,54	a*1	30,56	31,23	0,67	b*1	29,9	30,77	0,87	1,22	
	L*2	57,96	58,78	0,82	a*2	31,03	30,84	-0,19	b*2	30,35	30,41	0,06	0,84	
	L*3	58,45	58,65	0,2	a*3	31,01	30,6	-0,41	b*3	29,94	30,47	0,53	0,70	
	L*Av	58,46	58,62	0,16	a*Av	30,87	30,89	0,02	b*Av	30,06	30,55	0,49	0,92	*0,27*
Inhibitor C	L*1	54,8	54,51	-0,29	a*1	33,39	33,95	0,56	b*1	27,01	27,29	0,28	0,69	
	L*2	54,25	55,54	1,29	a*2	33,89	33,25	-0,64	b*2	27,05	27,83	0,78	1,64	
	L*3	55,52	53,92	-1,6	a*3	33,44	35,18	1,74	b*3	26,95	27,25	0,3	2,38	
	L*Av	54,86	54,66	-0,20	a*Av	33,57	34,13	0,55	b*Av	27,00	27,46	0,45	1,57	*0,85*
Inhibitor D	L*1	57,05	57,2	0,15	a*1	31,74	32,35	0,61	b*1	30,89	30,46	-0,43	0,76	
	L*2	56,79	57,37	0,58	a*2	31,24	32,58	1,34	b*2	29,85	30,01	0,16	1,47	
	L*3	57,4	56,78	-0,62	a*3	31,19	31,22	0,03	b*3	30,37	29,98	-0,39	0,73	
	L*Av	57,08	57,12	0,04	a*Av	31,39	32,05	0,66	b*Av	30,37	30,15	-0,22	0,99	*0,42*

Treated samples	L*	before	After 400h	ΔL*	a*	before	After 400h	Δa*	b*	before	After 400h	Δb*	ΔE	Standard deviation
Inhibitor E	L*1	57,41	58,13	0,72	a*1	34,07	33,85	-0,22	b*1	30,65	31,07	0,42	0,86	
	L*2	58,3	58,54	0,24	a*2	32,74	32,95	0,21	b*2	30,82	30,82	0	0,32	
	L*3	57,07	59,08	2,01	a*3	34,51	32,9	-1,61	b*3	31,13	31,01	-0,12	2,58	
	L*Av	57,59	58,58	0,99	a*Av	33,77	33,23	-0,54	b*Av	30,87	30,97	0,1	1,25	*1,18*
Inhibitor F	L*1	59,27	58,96	-0,31	a*1	34,66	34,39	-0,27	b*1	32,81	32,62	-0,19	0,45	
	L*2	58,26	59,33	1,07	a*2	34,67	34,55	-0,12	b*2	32,96	32,31	-0,65	1,26	
	L*3	58,5	58,96	0,46	a*3	34,91	34,15	-0,76	b*3	32,33	32,78	0,45	1,00	
	L*Av	58,68	59,08	0,41	a*Av	34,75	34,36	-0,38	b*Av	32,7	32,57	-0,13	0,90	*0,41*
Inhibitor G	L*1	59,26	59,01	-0,25	a*1	31,91	31,37	-0,54	b*1	32,55	31,82	-0,73	0,94	
	L*2	59,79	58,56	-1,23	a*2	31,21	31,97	0,76	b*2	31,93	32,11	0,18	1,46	
	L*3	57,94	58,06	0,12	a*3	32,23	31,81	-0,42	b*3	32,04	31,55	-0,49	0,66	
	L*Av	59,00	58,54	-0,45	a*Av	31,78	31,72	-0,07	b*Av	32,17	31,83	-0,35	1,02	*0,41*
Inhibitor H	L*1	58,71	59,33	0,62	a*1	31,28	30,37	-0,91	b*1	31,4	31,76	0,36	1,16	
	L*2	58,49	59,21	0,72	a*2	31,8	31,4	-0,4	b*2	31,23	31,23		0,82	
	L*3	61,01	59,57	-1,44	a*3	28,89	31,24	2,35	b*3	31,64	31,55	-0,09	2,76	
	L*Av	59,40	59,37	-0,03	a*Av	30,66	31,00	0,35	b*Av	31,42	31,51	0,135	1,58	*1,03*
Inhibitor I	L*1	59,14	59,25	0,11	a*1	29,36	29,16	-0,2	b*1	29,12	29,32	0,2	0,30	
	L*2	59,74	58,5	-1,24	a*2	28,85	29,23	0,38	b*2	28,17	29,9	1,73	2,16	
	L*3	58,37	59,17	0,8	a*3	30,83	28,64	-2,19	b*3	29,56	29	-0,56	2,40	
	L*Av	59,08	58,97	-0,11	a*Av	29,68	29,01	-0,67	b*Av	28,95	29,41	0,46	1,62	*1,15*

C.4.13 Colourimetric measurements of Combination 3 dyed samples exposed for 260 h at 50°C

Treated samples	L*	before	after260h	ΔL*	a*	before	after 260h	Δa*	b*	before	after 260h	Δb*	ΔE	Standard deviation
Blank	L*1	32,86	31,58	-1,28	a*1	50,07	48,16	-1,91	b*1	7,91	6,98	-0,93	2,48	
	L*2	31,76	31,33	-0,43	a*2	49,86	47,79	-2,07	b*2	9,14	7,74	-1,4	2,54	
	L*3	31,83	31,49	-0,34	a*3	49,8	48,19	-1,61	b*3	8,61	7,06	-1,55	2,26	
	L*Av	32,15	31,47	-0,68	a*Av	49,91	48,05	-1,86	b*Av	8,55	7,26	-1,29	2,43	0,15
Inhibitor A	L*1	33,68	34,55	0,87	a*1	50,88	51,21	0,33	b*1	7,4	5,42	-1,98	2,19	
	L*2	33,65	35,51	1,86	a*2	50,07	51,93	1,86	b*2	7,35	4,22	-3,13	4,09	
	L*3	34,79	33,74	-1,05	a*3	50,52	50,83	0,31	b*3	6,21	6,19	-0,02	1,09	
	L*Av	34,04	34,60	0,56	a*Av	50,49	51,32	0,83	b*Av	6,99	5,28	-1,71	2,46	1,51
Inhibitor B	L*1	33,45	32,6	-0,85	a*1	48,62	46,76	-1,86	b*1	7,18	7,05	-0,13	2,05	
	L*2	34,4	32,97	-1,43	a*2	48,46	46,43	-2,03	b*2	6,4	6,92	0,52	2,54	
	L*3	33,14	32,36	-0,78	a*3	47,77	46,58	-1,19	b*3	6,89	6,67	-0,22	1,44	
	L*Av	33,663	32,643	-1,020	a*Av	48,283	46,590	-1,693	b*Av	6,823	6,880	0,057	2,01	0,55
Inhibitor C	L*1	37,44	34,19	-3,25	a*1	43,86	45,56	1,7	b*1	3,01	3,92	0,91	3,78	
	L*2	37,49	36,22	-1,27	a*2	44,5	42,85	-1,65	b*2	3,54	2,84	-0,7	2,20	
	L*3	37,64	36,54	-1,1	a*3	44,26	44,76	0,5	b*3	2,97	2,6	-0,37	1,26	
	L*Av	37,52	35,65	-1,87	a*Av	44,21	44,39	0,18	b*Av	3,17	3,12	-0,05	2,41	1,27
Inhibitor D	L*1	30,83	30,07	-0,76	a*1	49,39	47,35	-2,04	b*1	8,26	6,56	-1,7	2,76	
	L*2	30,33	30,89	0,56	a*2	48,96	46,64	-2,32	b*2	7,62	5,75	-1,87	3,03	
	L*3	30,97	30,99	0,02	a*3	48,04	46,43	-1,61	b*3	7,63	5,68	-1,95	2,53	
	L*Av	30,71	30,65	-0,06	a*Av	48,80	46,81	-1,99	b*Av	7,84	6,00	-1,84	2,77	0,25

Treated samples	L*	before	after260h	ΔL*	a*	before	after 260h	Δa*	b*	before	after 260h	Δb*	ΔE	Standard deviation
Inhibitor E	L*1	33,71	32,24	-1,47	a*1	49,58	48,05	-1,53	b*1	8,23	8,33	0,1	2,12	
	L*2	33,87	32,54	-1,33	a*2	49,1	47,26	-1,84	b*2	7,96	6,92	-1,04	2,50	
	L*3	33,26	33,55	0,29	a*3	49,31	49,35	0,04	b*3	8,51	6,09	-2,42	2,44	
	L*Av	33,61	32,78	-0,84	a*Av	49,33	48,22	-1,11	b*Av	8,23	7,11	-1,12	2,35	0,20
Inhibitor F	L*1	31,89	30,64	-1,25	a*1	46,42	46,55	0,13	b*1	8,14	7,76	-0,38	1,31	
	L*2	32,24	30,16	-2,08	a*2	48,03	46,89	-1,14	b*2	7,77	7,83	0,06	2,37	
	L*3	31,72	31,33	-0,39	a*3	47,28	47,39	0,11	b*3	7,99	7,17	-0,82	0,91	
	L*Av	31,95	30,71	-1,24	a*Av	47,24	46,94	-0,30	b*Av	7,97	7,59	-0,38	1,53	0,75
Inhibitor G	L*1	31,98	31,81	-0,17	a*1	49,71	48,07	-1,64	b*1	7,28	5,52	-1,76	2,41	
	L*2	32,48	32,69	0,21	a*2	49,43	48,45	-0,98	b*2	6,11	5,2	-0,91	1,35	
	L*3	32,25	32,49	0,24	a*3	49,11	48,64	-0,47	b*3	6,97	5,22	-1,75	1,83	
	L*Av	32,24	32,33	0,09	a*Av	49,42	48,39	-1,03	b*Av	6,79	5,31	-1,47	1,86	0,53
Inhibitor H	L*1	32,45	31,42	-1,03	a*1	48,01	46,38	-1,63	b*1	7,13	7,29	0,16	1,93	
	L*2	33,13	31,78	-1,35	a*2	48,4	46,85	-1,55	b*2	7,09	7,32	0,23	2,07	
	L*3	31,6	32,33	0,73	a*3	48,19	47,12	-1,07	b*3	8,71	6,18	-2,53	2,84	
	L*Av	32,39	31,84	-0,55	a*Av	48,20	46,78	-1,42	b*Av	7,64	6,93	-0,71	2,28	0,49
Inhibitor I	L*1	33,36	31,92	-1,44	a*1	48,97	49,47	0,5	b*1	6,52	7,02	0,5	1,60	
	L*2	32,67	32,61	-0,06	a*2	50,46	48,68	-1,78	b*2	8,09	6,13	-1,96	2,65	
	L*3	33,01	32,73	-0,28	a*3	49,14	48,94	-0,2	b*3	6,99	4,28	-2,71	2,73	
	L*Av	33,01	32,42	-0,59	a*Av	49,52	49,03	-0,49	b*Av	7,2	5,81	-1,39	2,33	0,63

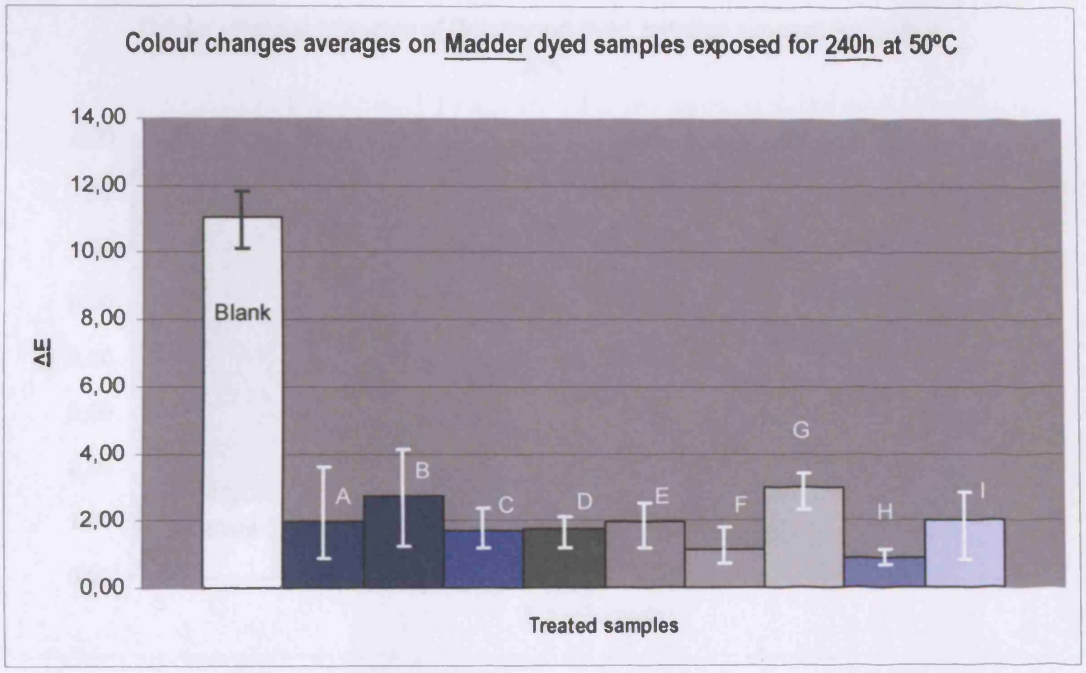
C.4.14 Colourimetric measurements of Combination 3 dyed samples exposed for 400 h at 50°C

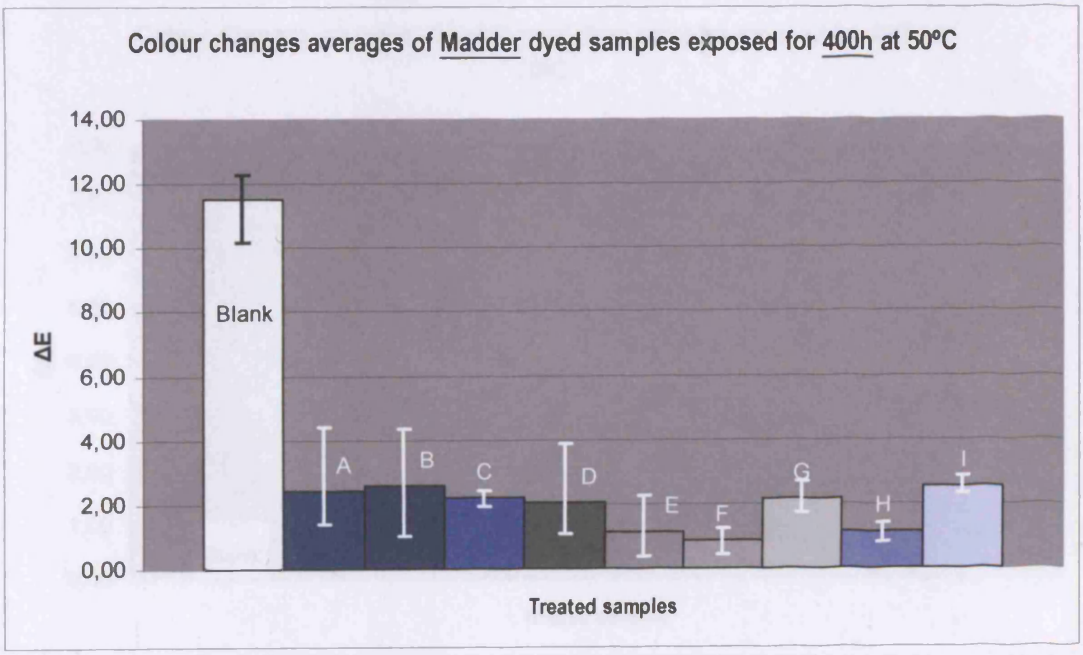
Treated samples	L*	before	after 400h	ΔL*	a*	before	after 400h	Δa*	b*	before	after 400h	Δb*	ΔE	Standard deviation
Blank	L*1	32,86	32,16	-0,7	a*1	50,07	48,63	-1,44	b*1	7,91	8,82	0,91	1,84	
	L*2	31,76	31,69	-0,07	a*2	49,86	48,56	-1,3	b*2	9,14	8,85	-0,29	1,33	
	L*3	31,83	31,93	0,1	a*3	49,8	48,35	-1,45	b*3	8,61	8,48	-0,13	1,46	
	L*Av	32,15	31,93	-0,22	a*Av	49,91	48,51	-1,40	b*Av	8,55	8,72	0,16	1,54	*0,26*
Inhibitor A	L*1	33,68	35,82	2,14	a*1	50,88	51,8	0,92	b*1	7,4	5,96	-1,44	2,74	
	L*2	33,65	34,43	0,78	a*2	50,07	51,86	1,79	b*2	7,35	7,47	0,12	1,96	
	L*3	34,79	36,08	1,29	a*3	50,52	51,87	1,35	b*3	6,21	5,66	-0,55	1,95	
	L*Av	34,04	35,44	1,40	a*Av	50,49	51,84	1,35	b*Av	6,99	6,36	-0,62	2,21	*0,45*
Inhibitor B	L*1	33,45	33,37	-0,08	a*1	48,62	47,45	-1,17	b*1	7,18	7,5	0,32	1,22	
	L*2	34,4	34,91	0,51	a*2	48,46	47,74	-0,72	b*2	6,4	6,14	-0,26	0,92	
	L*3	33,14	33,07	-0,07	a*3	47,77	47,32	-0,45	b*3	6,89	9	2,11	2,16	
	L*Av	33,66	33,78	0,12	a*Av	48,28	47,50	-0,78	b*Av	6,82	7,55	0,72	1,43	*0,65*
Inhibitor C	L*1	37,44	36,5	-0,94	a*1	43,86	45,9	2,04	b*1	3,01	4,15	1,14	2,52	
	L*2	37,49	36,53	-0,96	a*2	44,5	44,52	0,02	b*2	3,54	3,8	0,26	0,99	
	L*3	37,64	36,71	-0,93	a*3	44,26	44,13	-0,13	b*3	2,97	3,53	0,56	1,09	
	L*Av	37,52	36,58	-0,94	a*Av	44,21	44,85	0,64	b*Av	3,17	3,83	0,65	1,54	*0,85*
Inhibitor D	L*1	30,83	30,5	-0,33	a*1	49,39	47,66	-1,73	b*1	8,26	7,75	-0,51	1,83	
	L*2	30,33	30,78	0,45	a*2	48,96	48,03	-0,93	b*2	7,62	7,65	0,03	1,03	
	L*3	30,97	31,32	0,35	a*3	48,04	46	-2,04	b*3	7,63	6,96	-0,67	2,18	
	L*Av	30,71	30,87	0,16	a*Av	48,80	47,23	-1,57	b*Av	7,84	7,45	-0,38	1,68	*0,59*

Treated samples	L*	before	after 400h	ΔL*	a*	before	after 400h	Δa*	b*	before	after 400h	Δb*	ΔE	Standard deviation
Inhibitor E	L*1	33,71	33,84	0,13	a*1	49,58	48,5	-1,08	b*1	8,23	7,91	-0,32	1,13	
	L*2	33,87	34,05	0,18	a*2	49,1	48,4	-0,7	b*2	7,96	8,08	0,12	0,73	
	L*3	33,26	33,46	0,2	a*3	49,31	48,93	-0,38	b*3	8,51	8,6	0,09	0,44	
	L*Av	33,61	33,78	0,17	a*Av	49,33	48,61	-0,72	b*Av	8,23	8,20	-0,04	0,77	*0,35*
Inhibitor F	L*1	31,89	30,82	-1,07	a*1	46,42	47,46	1,04	b*1	8,14	8,82	0,68	1,64	
	L*2	32,24	31,29	-0,95	a*2	48,03	47,96	-0,07	b*2	7,77	8,07	0,3	1,00	
	L*3	31,72	30,27	-1,45	a*3	47,28	46,65	-0,63	b*3	7,99	8,94	0,95	1,84	
	L*Av	31,95	30,79	-1,16	a*Av	47,24	47,36	0,11	b*Av	7,97	8,61	0,64	1,49	*0,44*
Inhibitor G	L*1	31,98	32,91	0,93	a*1	49,71	48,9	-0,81	b*1	7,28	6,42	-0,86	1,50	
	L*2	32,48	32,57	0,09	a*2	49,43	49,09	-0,34	b*2	6,11	6,79	0,68	0,77	
	L*3	32,25	33,28	1,03	a*3	49,11	49,21	0,1	b*3	6,97	6,48	-0,49	1,14	
	L*Av	32,24	32,92	0,68	a*Av	49,42	49,07	-0,35	b*Av	6,79	6,56	-0,22	1,14	*0,37*
Inhibitor H	L*1	32,45	32,06	-0,39	a*1	48,01	47,59	-0,42	b*1	7,13	7,21	0,08	0,58	
	L*2	33,13	32,24	-0,89	a*2	48,4	47,74	-0,66	b*2	7,09	8,58	1,49	1,86	
	L*3	31,6	32,33	0,73	a*3	48,19	47,33	-0,86	b*3	8,71	7,62	-1,09	1,57	
	L*Av	32,39	32,21	-0,18	a*Av	48,20	47,55	-0,65	b*Av	7,64	7,80	0,16	1,33	*0,67*
Inhibitor I	L*1	33,36	31,89	-1,47	a*1	48,97	49,04	0,07	b*1	6,52	11,08	4,56	4,79	
	L*2	32,67	33,42	0,75	a*2	50,46	49,3	-1,16	b*2	8,09	5,81	-2,28	2,67	
	L*3	33,01	33,48	0,47	a*3	49,14	48,49	-0,65	b*3	6,99	6,98	-0,01	0,80	
	L*Av	33,01	32,93	-0,08	a*Av	49,52	48,94	-0,58	b*Av	7,20	7,96	0,76	2,75	*2,00*

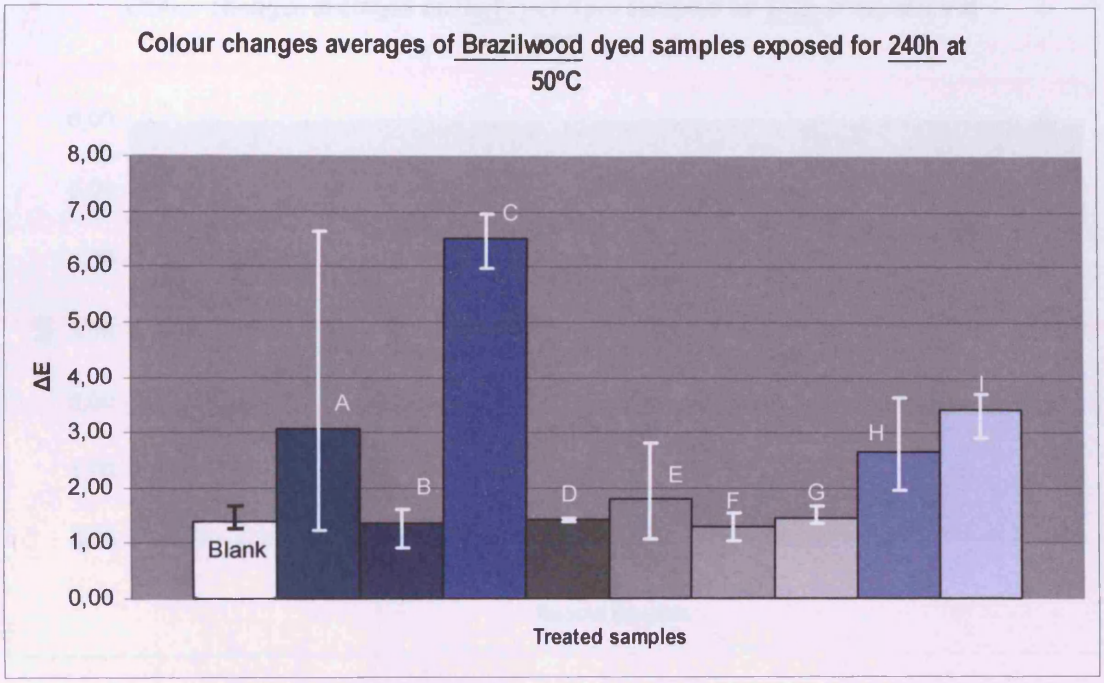
C.5 Colour changes on samples exposed at 50°C

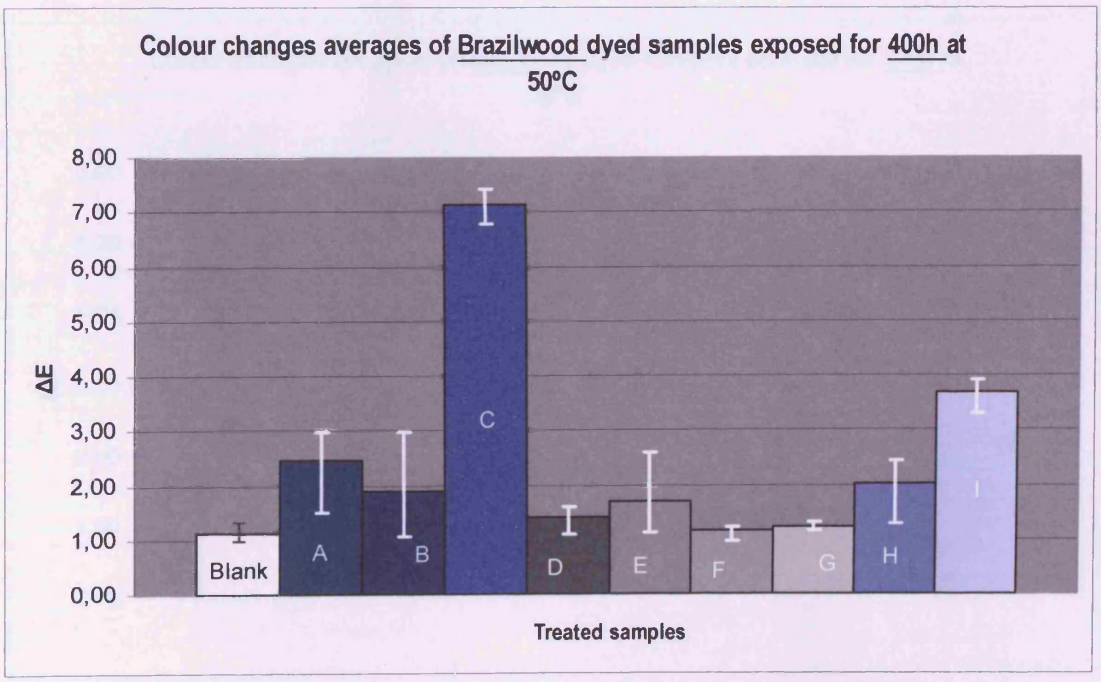
C.5.1 Colour changes on Madder dyed samples



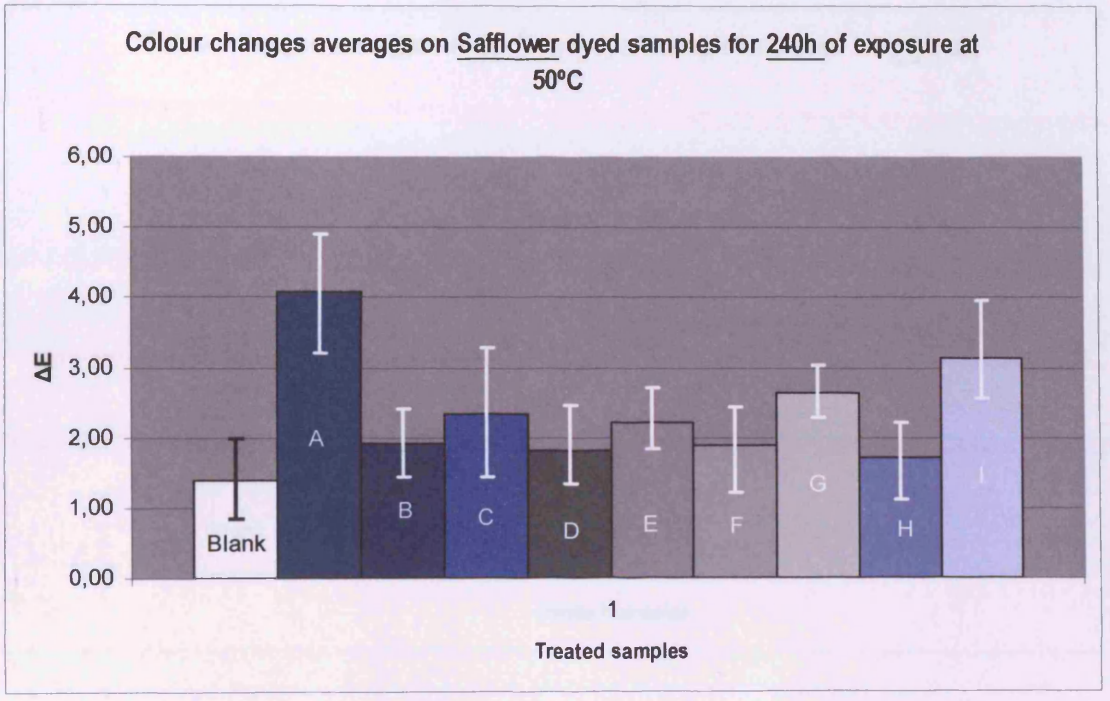


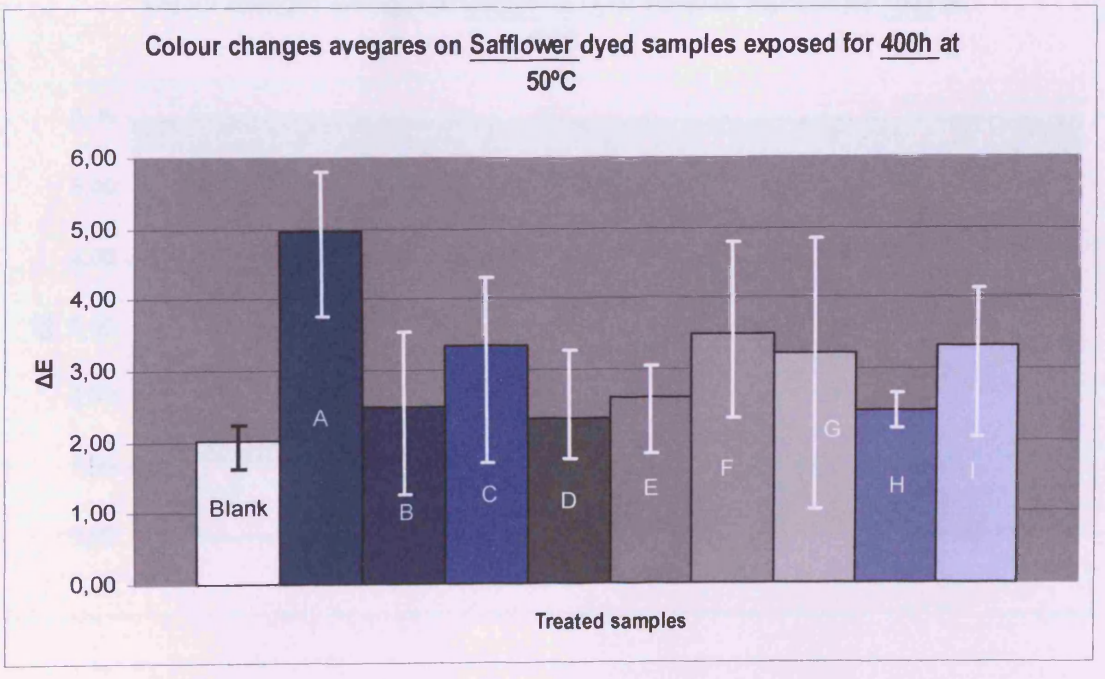
C.5.2 Colour changes on Brazilwood dyed samples



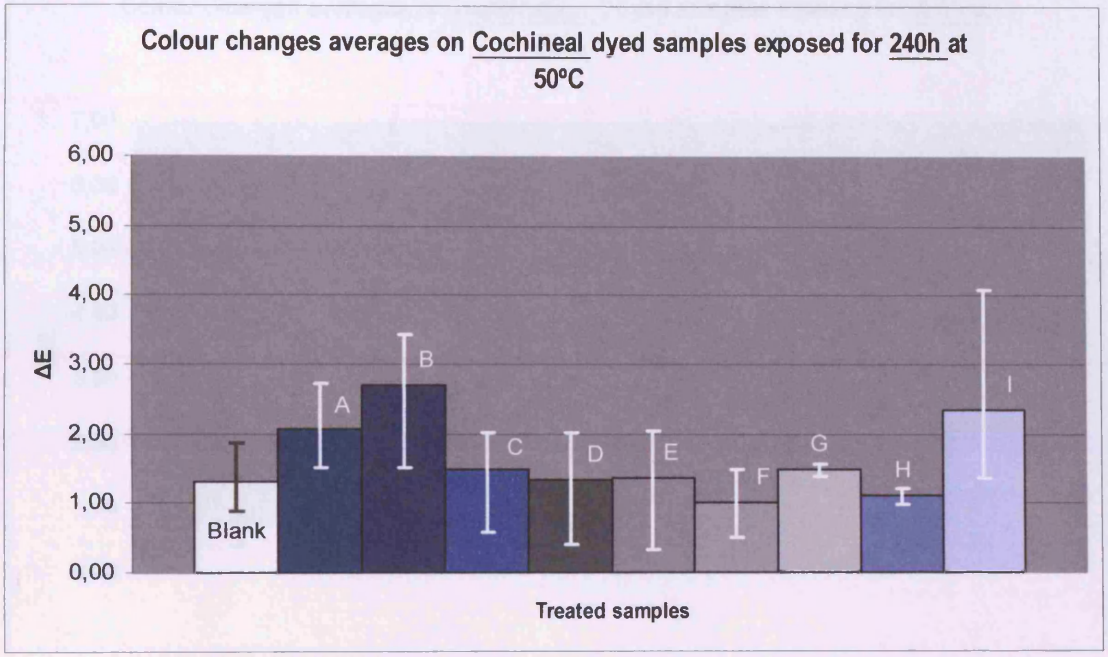


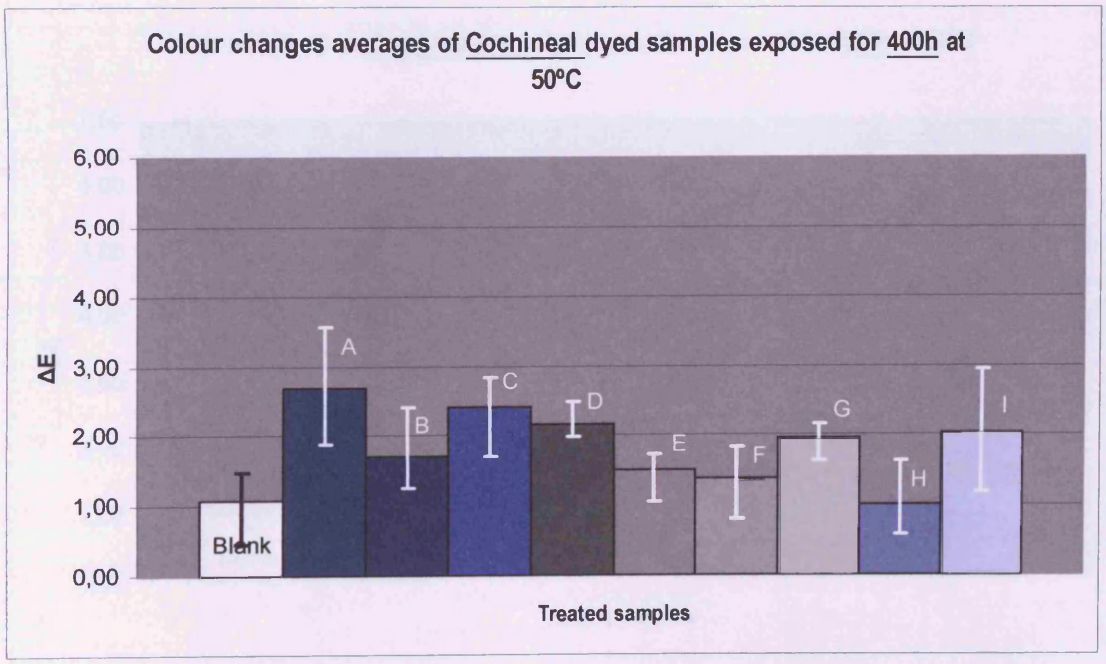
C.5.3 Colour changes of Safflower dyed samples



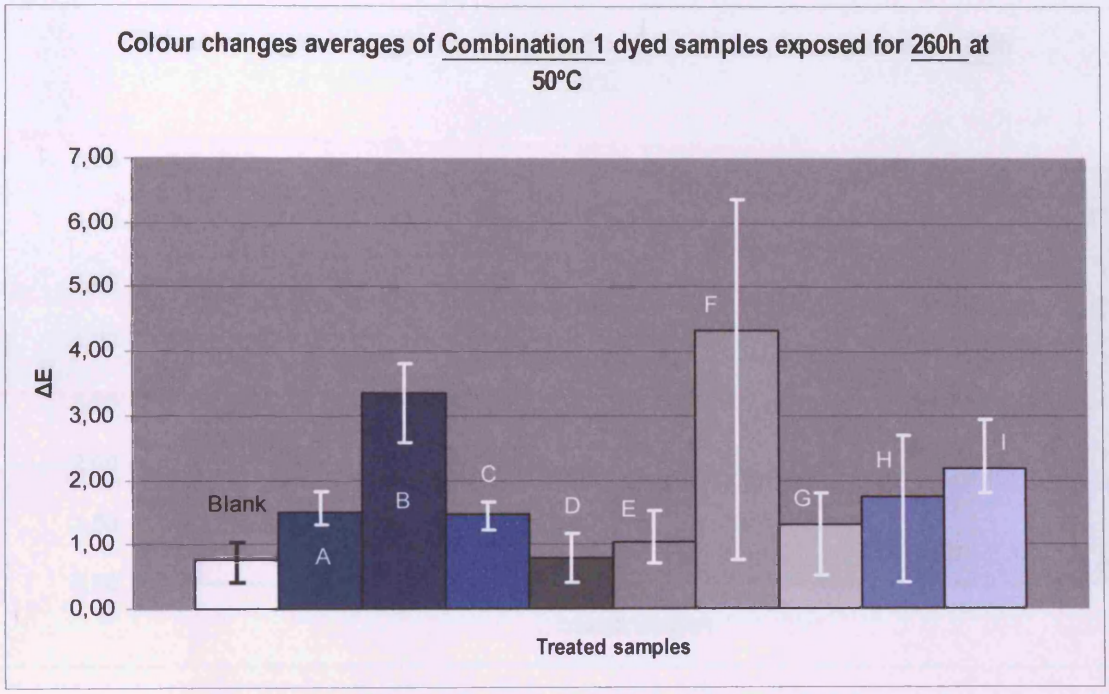


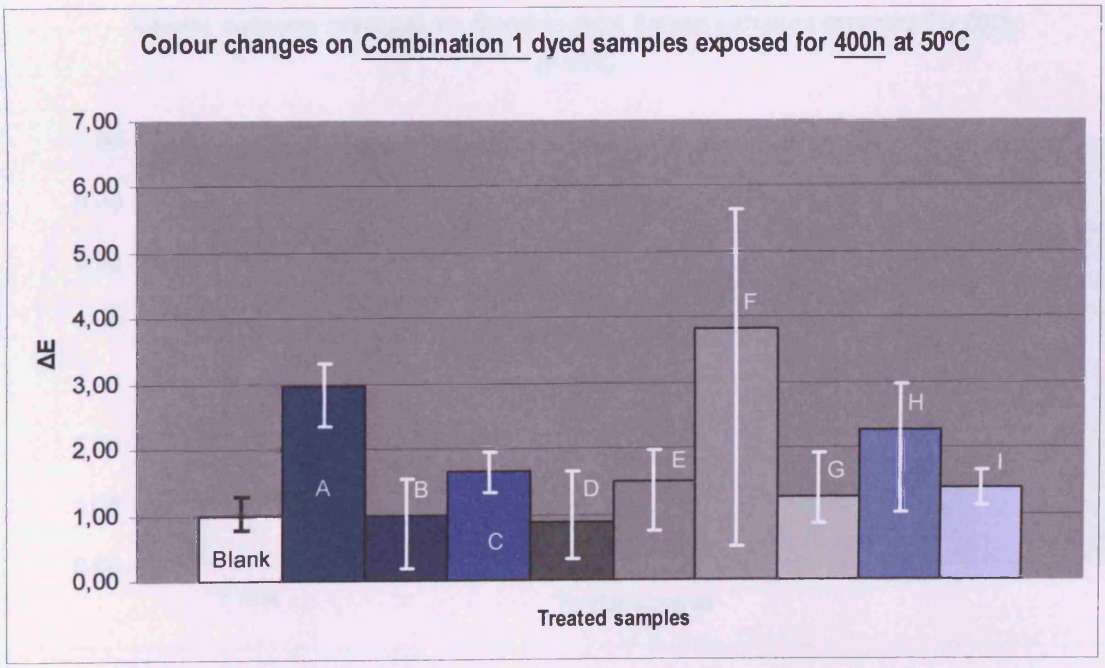
C.5.4 Colour changes of Cochineal dyed samples



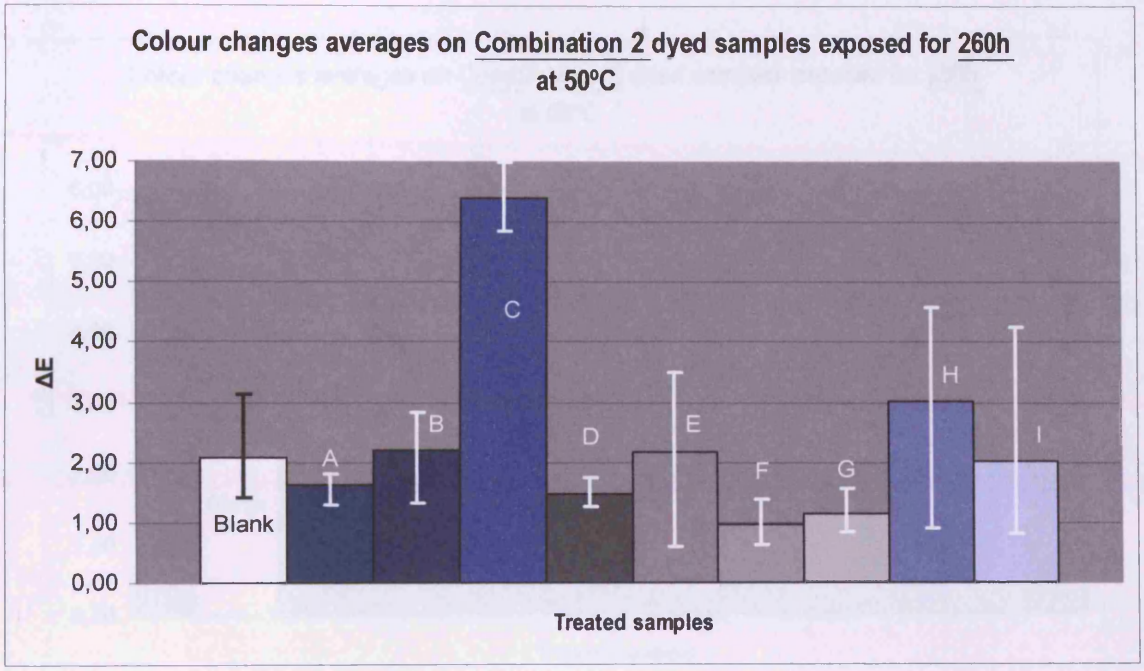


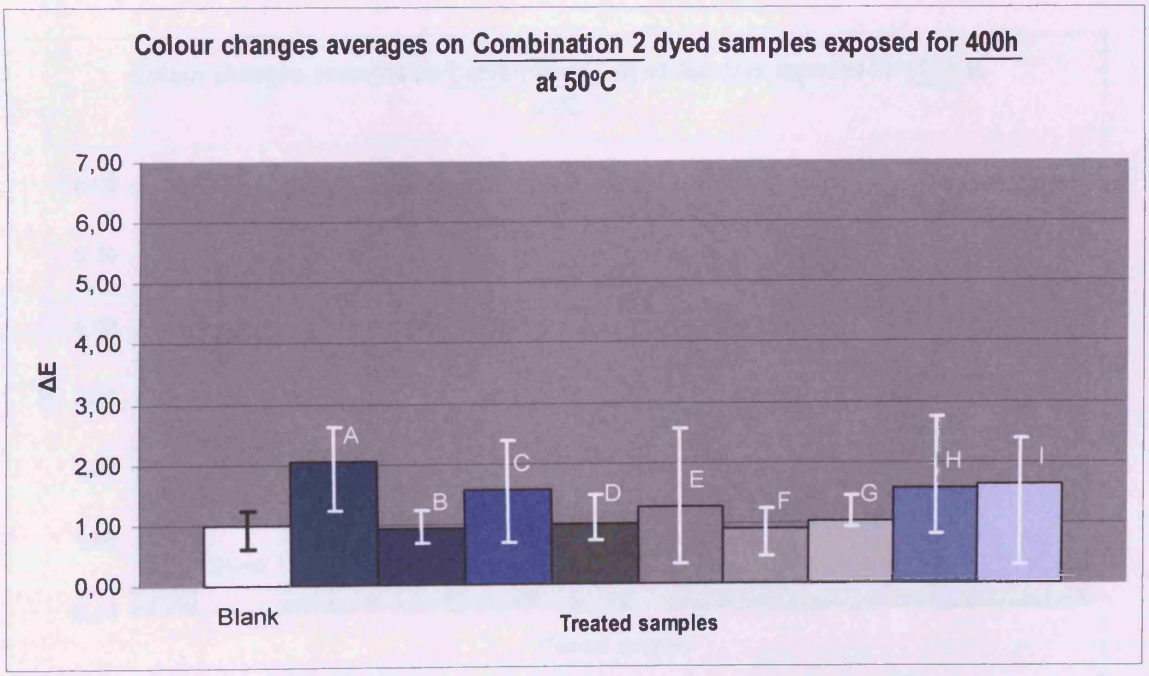
C.5.5 Colour changes of Combination 1 dyed samples



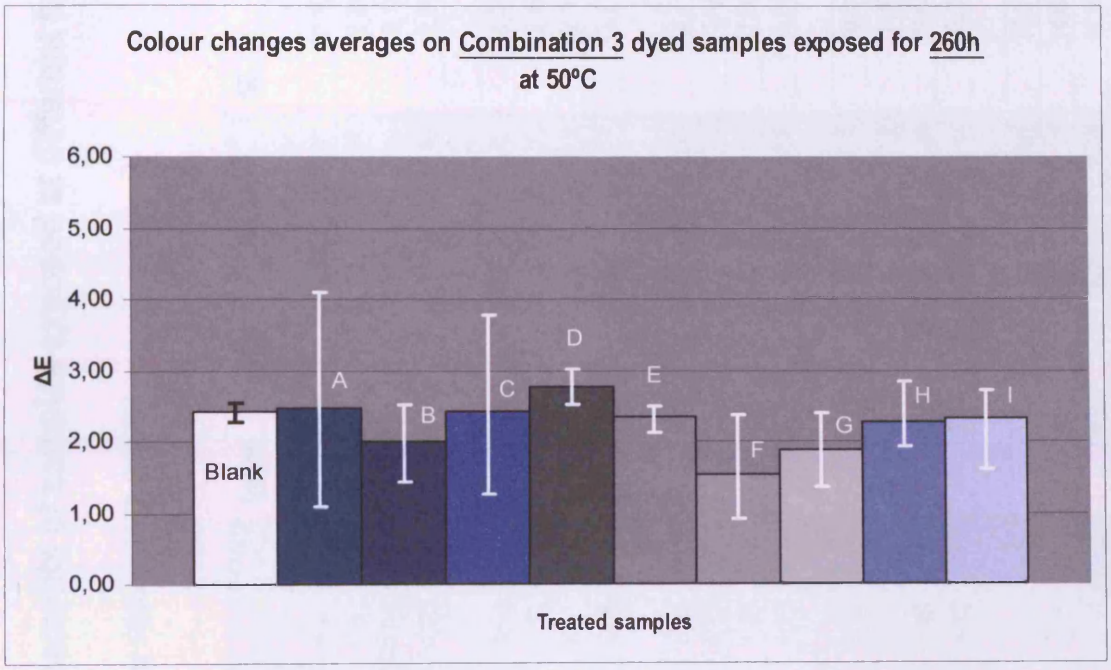


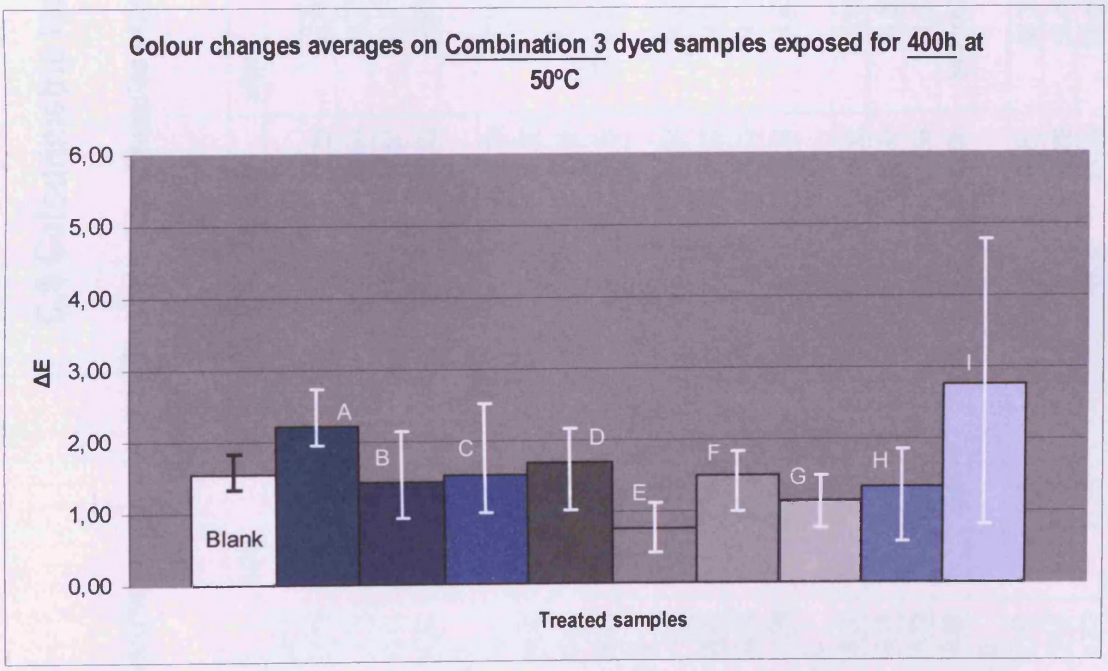
C.5.6 Colour changes of Combination 2 dyed samples





C.5.7 Colour changes of Combination 3 dyed samples





C.6 Colourimetric measurements of samples exposed at different humidity levels

C.6.1 Colourimetric measurements of Brazilwood dyed samples exposed for 100h at 35°C, 30%RH

	before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	*Standard deviation*
	Blank sample												
L*1	19,76	26,3	6,54	a*1	51,39	54,84	3,45	b*1	34,06	40,95	6,89	10,10	*0,52*
L*2	19,9	26,36	6,46	a*2	54,94	54,28	-0,66	b*2	34,5	41,04	6,54	9,21	
L*3	20,19	26,49	6,3	a*3	51,87	54,95	3,08	b*3	34,79	40,69	5,9	9,16	
L*Av	19,95	26,38	6,43	a*Av	52,73	54,69	1,95	b*Av	34,45	40,89	6,44	9,31	
	Inhibitor A												
L*1	18,11	29,91	11,8	a*1	49,75	57,91	8,16	b*1	31,21	30,82	-0,39	14,35	*1,02*
L*2	18,97	29,62	10,65	a*2	50,56	57,02	6,46	b*2	32,69	32,13	-0,56	12,46	
L*3	18,56	29,4	10,84	a*3	50,18	56,75	6,57	b*3	31,99	32,89	0,9	12,70	
L*Av	18,54	29,64	11,09	a*Av	50,16	57,22667	7,06	b*Av	31,96	31,94	-0,01	13,15	
	Inhibitor B												
L*1	17,7	25,79	8,09	a*1	49,29	54,47	5,18	b*1	30,5	38,05	7,55	12,21	*0,58*
L*2	18,01	25,44	7,43	a*2	49,55	54,06	4,51	b*2	31,04	38,57	7,53	11,49	
L*3	18,23	26,2	7,97	a*3	49,78	54,76	4,98	b*3	31,41	37,22	5,81	11,04	
L*Av	17,98	25,81	7,83	a*Av	49,54	54,43	4,89	b*Av	30,98	37,94	6,96	11,56	
	Inhibitor C												
L*1	18,38	27,1	8,72	a*1	49,82	55,06	5,24	b*1	31,68	32,58	0,9	10,21	*0,15*
L*2	18,16	26,97	8,81	a*2	49,63	54,88	5,25	b*2	31,3	33,42	2,12	10,47	
L*3	18,12	26,33	8,21	a*3	49,55	54,51	4,96	b*3	31,22	35,46	4,24	10,48	
L*Av	18,22	26,8	8,58	a*Av	49,66	54,81667	5,15	b*Av	31,4	33,82	2,42	10,29	
	Inhibitor D												
L*1	17,37	27,6	10,23	a*1	48,87	55,35	6,48	b*1	29,94	37,95	8,01	14,51	*0,23*
L*2	17,2	27,78	10,58	a*2	48,69	55,42	6,73	b*2	29,65	37,53	7,88	14,80	
L*3	17,2	27,59	10,39	a*3	48,73	55,29	6,56	b*3	29,64	38,2	8,56	14,97	
L*Av	17,25	27,65	10,4	a*Av	48,76	55,35	6,59	b*Av	29,74333	37,89	8,15	14,7	

	before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	*Standard deviation*
	Inhibitor E												
L*1	17,06	22,59	5,53	a*1	48,7	51,55	2,85	b*1	29,4	38,94	9,54	11,38	*0,44*
L*2	17,07	22,5	5,43	a*2	48,72	51,38	2,66	b*2	29,42	38,77	9,35	11,13	
L*3	17,34	22,48	5,14	a*3	49,07	51,45	2,38	b*3	29,88	38,74	8,86	10,51	
L*Av	17,1	22,52	5,36	a*Av	48,83	51,46	2,63	b*Av	29,56	38,81	9,25	11,01	
	Inhibitor F												
L*1	18,41	22,5	4,09	a*1	50,02	51,39	1,37	b*1	31,75	38,78	7,03	8,24	*0,67*
L*2	18,19	22	3,81	a*2	49,8	51,08	1,28	b*2	31,35	37,91	6,56	7,69	
L*3	18,69	22,12	3,43	a*3	50,27	51,11	0,84	b*3	32,2	38,13	5,93	6,90	
L*Av	18,43	22,20	3,77	a*Av	50,03	51,19	1,16	b*Av	31,76	38,27	6,50	7,61	
	Inhibitor G												
L*1	20,49	26,34	5,85	a*1	52,1	54,36	2,26	b*1	35,32	40,82	5,5	8,34	*0,52*
L*2	20,75	26,29	5,54	a*2	52,34	54,38	2,04	b*2	35,75	40,17	4,42	7,37	
L*3	20,63	26,57	5,94	a*3	52,2	54,62	2,42	b*3	35,56	39,45	3,89	7,50	
L*Av	20,62	26,4	5,77	a*Av	52,21	54,45	2,24	b*Av	35,54	40,14	4,60	7,71	
	Inhibitor H												
L*1	17,39	22,58	5,19	a*1	49,08	51,51	2,43	b*1	29,97	38,91	8,94	10,61	*0,22*
L*2	17,4	22,53	5,13	a*2	49,08	51,48	2,4	b*2	29,99	38,82	8,83	10,49	
L*3	17,37	22,34	4,97	a*3	49,05	51,38	2,33	b*3	29,94	38,51	8,57	10,17	
L*Av	17,38	22,48	5,09	a*Av	49,07	51,45	2,38	b*Av	29,96	38,74	8,78	10,42	
	Inhibitor I												
L*1	18,01	24,26	6,25	a*1	49,46	52,79	3,33	b*1	31,04	40,16	9,12	11,54	*0,64*
L*2	17,87	24	6,13	a*2	49,3	52,48	3,18	b*2	30,8	40,66	9,86	12,03	
L*3	18,43	24,15	5,72	a*3	49,84	52,71	2,87	b*3	31,76	40,4	8,64	10,75	
L*Av	18,10	24,13	6,03	a*Av	49,53	52,66	3,12	b*Av	31,2	40,40	9,20	11,44	

C.6.2 Colourimetric measurements of Brazilwood dyed samples exposed for 100h at 35°C, 50%RH

	before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	*Standard deviation*
	Blank sample												
L*1	19,9	26,04	6,14	a*1	51,54	54,46	2,92	b*1	34,3	40,62	6,32	9,28	*0,31*
L*2	19,92	25,92	6	a*2	51,56	54,47	2,91	b*2	34,34	41,15	6,81	9,53	
L*3	20,15	25,84	5,69	a*3	51,81	54,38	2,57	b*3	34,73	42,41	7,68	9,90	
L*Av	19,99	25,93	5,94	a*Av	51,64	54,44	2,80	b*Av	34,46	41,39	6,94	9,55	
	Inhibitor A												
L*1	18,11	27,24	9,13	a*1	49,75	55,08	5,33	b*1	31,21	38,49	7,28	12,84	*1,05*
L*2	18,97	27,42	8,45	a*2	50,56	55,22	4,66	b*2	32,69	37,49	4,8	10,78	
L*3	18,56	27,3	8,74	a*3	50,18	55,17	4,99	b*3	31,99	37,38	5,39	11,42	
L*Av	18,55	27,32	8,77	a*Av	50,16	55,16	4,99	b*Av	31,96	37,79	5,82	11,65	
	Inhibitor B												
L*1	17,7	24,57	6,87	a*1	49,29	53,05	3,76	b*1	30,5	40,28	9,78	12,53	*1,00*
L*2	18,01	24,87	6,86	a*2	49,55	53,42	3,87	b*2	31,04	39,06	8,02	11,24	
L*3	18,23	24,52	6,29	a*3	49,78	53,07	3,29	b*3	31,41	39,22	7,81	10,55	
L*Av	17,98	24,65	6,67	a*Av	49,54	53,18	3,64	b*Av	30,98	39,52	8,54	11,43	
	Inhibitor C												
L*1	18,38	29,55	11,17	a*1	49,82	56,98	7,16	b*1	31,68	26,15	-5,53	14,37	*0,10*
L*2	18,16	29,65	11,49	a*2	49,63	57,1	7,47	b*2	31,3	26,44	-4,86	14,54	
L*3	18,12	29,42	11,3	a*3	49,55	56,89	7,34	b*3	31,22	26,26	-4,96	14,36	
L*Av	18,22	29,54	11,32	a*Av	49,67	56,99	7,32	b*Av	31,40	26,28	-5,12	14,42	
	Inhibitor D												
L*1	17,37	25,64	8,27	a*1	48,87	53,74	4,87	b*1	29,94	38,53	8,59	12,88	*0,18*
L*2	17,2	25,68	8,48	a*2	48,69	53,85	5,16	b*2	29,65	38,41	8,76	13,24	
L*3	17,2	25,65	8,45	a*3	48,73	53,82	5,09	b*3	29,64	38,27	8,63	13,11	
L*Av	17,26	25,66	8,40	a*Av	48,76	53,80	5,04	b*Av	29,74	38,40	8,66	13,08	

	Before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	*Standard deviation*
	Inhibitor E												
L*1	17,06	24,76	7,7	a*1	48,7	53,13	4,43	b*1	29,4	39,94	10,54	13,78	*0,25*
L*2	17,07	24,9	7,83	a*2	48,72	53,26	4,54	b*2	29,42	39,73	10,31	13,72	
L*3	17,34	25,19	7,85	a*3	49,07	53,56	4,49	b*3	29,88	39,66	9,78	13,32	
L*Av	17,16	24,95	7,79	a*Av	48,83	53,32	4,49	b*Av	29,57	39,78	10,21	13,61	
	Inhibitor F												
L*1	18,41	24,84	6,43	a*1	50,02	53,25	3,23	b*1	31,75	40,07	8,32	11,00	*0,77*
L*2	18,19	24,68	6,49	a*2	49,8	53,04	3,24	b*2	31,35	40,78	9,43	11,90	
L*3	18,69	24,84	6,15	a*3	50,27	53,26	2,99	b*3	32,2	39,99	7,79	10,37	
L*Av	18,43	24,79	6,36	a*Av	50,03	53,18	3,15	b*Av	31,77	40,28	8,51	11,08	
	Inhibitor G												
L*1	20,49	29,52	9,03	a*1	52,1	56,85	4,75	b*1	35,32	28,47	-6,85	12,29	*0,44*
L*2	20,75	29,39	8,64	a*2	52,34	56,73	4,39	b*2	35,75	29,01	-6,74	11,80	
L*3	20,63	29,33	8,7	a*3	52,2	56,66	4,46	b*3	35,56	29,67	-5,89	11,41	
L*Av	20,62	29,41	8,79	a*Av	52,21	56,75	4,53	b*Av	35,54	29,05	-6,49	11,83	
	Inhibitor H												
L*1	17,39	23,25	5,86	a*1	49,08	51,76	2,68	b*1	29,97	38,99	9,02	11,09	*0,25*
L*2	17,4	23,54	6,14	a*2	49,08	52,06	2,98	b*2	29,99	39,26	9,27	11,51	
L*3	17,37	23,62	6,25	a*3	49,05	52,18	3,13	b*3	29,94	38,52	8,58	11,07	
L*Av	17,39	23,47	6,08	a*Av	49,07	52,00	2,93	b*Av	29,97	38,92	8,96	11,22	
	Inhibitor I												
L*1	18,01	25,08	7,07	a*1	49,46	53,72	4,26	b*1	31,04	36,79	5,75	10,06	*0,37*
L*2	17,87	25,15	7,28	a*2	49,3	53,82	4,52	b*2	30,8	36,41	5,61	10,24	
L*3	18,43	25,43	7	a*3	49,84	54,02	4,18	b*3	31,76	36,71	4,95	9,54	
L*Av	18,10	25,22	7,12	a*Av	49,53	53,85	4,32	b*Av	31,20	36,64	5,44	9,94	

C.6.3 Colourimetric measurements of Brazilwood dyed samples exposed for 100h at 35°C, 80%RH

	before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	*Standard deviation*
	Blank sample												
L*1	19,9	29,82	9,92	a*1	51,54	55,75	4,21	b*1	34,3	27,82	-6,48	12,57	*0,67*
L*2	19,92	29,85	9,93	a*2	51,56	55,7	4,14	b*2	34,34	27,58	-6,76	12,71	
L*3	20,15	29,64	9,49	a*3	51,81	55,22	3,41	b*3	34,73	29,22	-5,51	11,49	
L*Av	19,99	29,77	9,78	a*Av	51,64	55,56	3,92	b*Av	34,46	28,21	-6,25	12,25	
	Inhibitor A												
L*1	18,11	30,35	12,24	a*1	49,75	56,21	6,46	b*1	31,21	25,98	-5,23	14,80	*0,29*
L*2	18,97	30,56	11,59	a*2	50,56	56,04	5,48	b*2	32,69	25,96	-6,73	14,48	
L*3	18,56	30,87	12,31	a*3	50,18	55,52	5,34	b*3	31,99	25,15	-6,84	15,06	
L*Av	18,55	30,59	12,05	a*Av	50,16	55,92	5,76	b*Av	31,96	25,70	-6,27	14,75	
	Inhibitor B												
L*1	17,7	29,88	12,18	a*1	49,29	56,29	7	b*1	30,5	25,4	-5,1	14,95	*0,12*
L*2	18,01	29,99	11,98	a*2	49,55	56,4	6,85	b*2	31,04	24,73	-6,31	15,17	
L*3	18,23	29,96	11,73	a*3	49,78	56,38	6,6	b*3	31,41	24,71	-6,7	15,03	
L*Av	17,98	29,94	11,96	a*Av	49,54	56,36	6,82	b*Av	30,98	24,95	-6,04	15,03	
	Inhibitor C												
L*1	18,38	32,02	13,64	a*1	49,82	56,86	7,04	b*1	31,68	20,86	-10,82	18,78	*0,35*
L*2	18,16	31,93	13,77	a*2	49,63	57,08	7,45	b*2	31,3	20,08	-11,22	19,26	
L*3	18,12	32,05	13,93	a*3	49,55	57,07	7,52	b*3	31,22	19,89	-11,33	19,47	
L*Av	18,22	32	13,78	a*Av	49,67	57,00	7,34	b*Av	31,40	20,28	-11,12	19,17	
	Inhibitor D												
L*1	17,37	28,85	11,48	a*1	48,87	55,12	6,25	b*1	29,94	26,02	-3,92	13,65	*0,11*
L*2	17,2	28,67	11,47	a*2	48,69	55,07	6,38	b*2	29,65	26,54	-3,11	13,49	
L*3	17,2	28,78	11,58	a*3	48,73	55,17	6,44	b*3	29,64	26,17	-3,47	13,70	
L*Av	17,26	28,77	11,51	a*Av	48,76	55,12	6,36	b*Av	29,74	26,24	-3,5	13,61	

	before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	*Standard deviation*
	Inhibitor E												
L*1	17,06	23,48	6,42	a*1	48,7	51,45	2,75	b*1	29,4	39,91	10,51	12,62	*0,27*
L*2	17,07	23,54	6,47	a*2	48,72	51,52	2,8	b*2	29,42	39,87	10,45	12,61	
L*3	17,34	23,55	6,21	a*3	49,07	51,53	2,46	b*3	29,88	40,03	10,15	12,15	
L*Av	17,16	23,52	6,37	a*Av	48,83	51,50	2,67	b*Av	29,57	39,94	10,37	12,46	
	Inhibitor F												
L*1	18,41	24,63	6,22	a*1	50,02	52,63	2,61	b*1	31,75	40,09	8,34	10,73	*0,60*
L*2	18,19	24,52	6,33	a*2	49,8	52,51	2,71	b*2	31,35	40,35	9	11,33	
L*3	18,69	24,25	5,56	a*3	50,27	52,21	1,94	b*3	32,2	40,44	8,24	10,13	
L*Av	18,43	24,47	6,04	a*Av	50,03	52,45	2,42	b*Av	31,77	40,29	8,53	10,72	
	Inhibitor G												
L*1	20,49	28,38	7,89	a*1	52,1	54,23	2,13	b*1	35,32	29,56	-5,76	10,00	*0,29*
L*2	20,75	28,39	7,64	a*2	52,34	54,24	1,9	b*2	35,75	29,88	-5,87	9,82	
L*3	20,63	28,55	7,92	a*3	52,2	54,35	2,15	b*3	35,56	29,18	-6,38	10,39	
L*Av	20,62	28,44	7,82	a*Av	52,21	54,27	2,06	b*Av	35,54	29,54	-6,00	10,07	
	Inhibitor H												
L*1	17,39	25,04	7,65	a*1	49,08	53,06	3,98	b*1	29,97	34,64	4,67	9,81	*0,22*
L*2	17,4	25,32	7,92	a*2	49,08	53,15	4,07	b*2	29,99	34,94	4,95	10,19	
L*3	17,37	24,35	6,98	a*3	49,05	52,68	3,63	b*3	29,94	35,78	5,84	9,80	
L*Av	17,39	24,90	7,52	a*Av	49,07	52,96	3,89	b*Av	29,97	35,12	5,15	9,91	
	Inhibitor I												
L*1	18,01	29	10,99	a*1	49,46	55,44	5,98	b*1	31,04	25,31	-5,73	13,76	*0,28*
L*2	17,87	29,09	11,22	a*2	49,3	55,52	6,22	b*2	30,8	25,34	-5,46	13,94	
L*3	18,43	29,23	10,8	a*3	49,84	55,7	5,86	b*3	31,76	24,42	-7,34	14,31	
L*Av	18,10	29,11	11,00	a*Av	49,53	55,55	6,02	b*Av	31,20	25,02	-6,18	13,98	

C.6.4 Colourimetric measurements of Cochineal dyed samples exposed for 100h at 35°C, 35%RH

	before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	*Standard deviation*
	Blank sample												
L*1	15,22	16,39	1,17	a*1	46,91	48	1,09	b*1	26,24	28,25	2,01	2,57	*0,67*
L*2	14,82	16,31	1,49	a*2	46,47	47,92	1,45	b*2	25,54	28,11	2,57	3,31	
L*3	14,59	16,34	1,75	a*3	46,18	47,95	1,77	b*3	25,14	28,16	3,02	3,91	
L*Av	14,88	16,35	1,47	a*Av	46,52	47,96	1,44	b*Av	25,64	28,17	2,53	3,26	
	Inhibitor A												
L*1	12,63	15,01	2,38	a*1	43,76	46,45	2,69	b*1	21,77	25,87	4,1	5,45	*0,36*
L*2	12,59	14,73	2,14	a*2	43,7	46,14	2,44	b*2	21,7	25,38	3,68	4,91	
L*3	12,62	14,7	2,08	a*3	43,75	46,12	2,37	b*3	21,74	25,33	3,59	4,78	
L*Av	12,61	14,81	2,20	a*Av	43,74	46,24	2,50	b*Av	21,74	25,53	3,79	5,05	
	Inhibitor B												
L*1	12,41	14,03	1,62	a*1	43,16	45,2	2,04	b*1	21,39	24,17	2,78	3,81	*1,10*
L*2	11,89	14,28	2,39	a*2	42,51	45,48	2,97	b*2	20,48	24,6	4,12	5,61	
L*3	12,38	13,92	1,54	a*3	43,16	45,07	1,91	b*3	21,33	23,98	2,65	3,61	
L*Av	12,23	14,08	1,85	a*Av	42,94	45,25	2,31	b*Av	21,07	24,25	3,18	4,34	
	Inhibitor C												
L*1	12,19	16,34	4,15	a*1	43,08	47,93	4,85	b*1	21	28,16	7,16	9,59	*1,50*
L*2	11,47	16,36	4,89	a*2	42,14	47,94	5,8	b*2	19,76	28,2	8,44	11,35	
L*3	10,95	16,35	5,4	a*3	41,41	47,93	6,52	b*3	18,87	28,17	9,3	12,58	
L*Av	11,54	16,35	4,81	a*Av	42,21	47,93	5,72	b*Av	19,88	28,18	8,3	11,17	
	Inhibitor D												
L*1	12,23	13,51	1,28	a*1	43,37	44,45	1,08	b*1	21,07	23,27	2,2	2,76	*0,25*
L*2	12,17	13,41	1,24	a*2	43,3	44,31	1,01	b*2	20,98	23,11	2,13	2,66	
L*3	12,22	13,66	1,44	a*3	43,35	44,64	1,29	b*3	21,06	23,54	2,48	3,14	
L*Av	12,21	13,53	1,32	a*Av	43,34	44,47	1,13	b*Av	21,04	23,31	2,27	2,86	

	Before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	*Standard deviation*
	Inhibitor E												
L*1	10,98	11,86	0,88	a*1	41,91	42,74	0,83	b*1	18,93	20,43	1,5	1,93	*0,85*
L*2	11,09	11,64	0,55	a*2	42,03	42,48	0,45	b*2	19,1	20,05	0,95	1,19	
L*3	11,47	11,49	0,02	a*3	42,55	42,33	-0,22	b*3	19,77	19,8	0,03	0,22	
L*Av	11,18	11,66	0,48	a*Av	42,16	42,52	0,35	b*Av	19,27	20,09	0,83	1,02	
	Inhibitor F												
L*1	12,32	14,14	1,82	a*1	43,4	45,5	2,1	b*1	21,22	24,37	3,15	4,20	*1,12*
L*2	12,68	13,91	1,23	a*2	43,79	45,13	1,34	b*2	21,86	23,97	2,11	2,79	
L*3	13,02	13,9	0,88	a*3	44,17	45,12	0,95	b*3	22,44	23,94	1,5	1,98	
L*Av	12,67	13,98	1,31	a*Av	43,79	45,25	1,46	b*Av	21,84	24,09	2,25	2,99	
	Inhibitor G												
L*1	14,76	14,98	0,22	a*1	46,22	46,42	0,2	b*1	25,43	25,82	0,39	0,49	*0,22*
L*2	14,69	15,01	0,32	a*2	46,18	46,44	0,26	b*2	25,32	25,87	0,55	0,69	
L*3	14,82	14,95	0,13	a*3	46,32	46,36	0,04	b*3	25,54	25,75	0,21	0,25	
L*Av	14,76	14,98	0,22	a*Av	46,24	46,41	0,17	b*Av	25,43	25,81	0,38	0,47	
	Inhibitor H												
L*1	14,2	13,79	-0,41	a*1	45,49	44,86	-0,63	b*1	24,46	23,76	-0,7	1,03	*0,41*
L*2	13,72	13,52	-0,2	a*2	44,92	44,54	-0,38	b*2	23,65	23,29	-0,36	0,56	
L*3	13,6	13,55	-0,05	a*3	44,75	44,57	-0,18	b*3	23,43	23,35	-0,08	0,20	
L*Av	13,84	13,62	-0,22	a*Av	45,05	44,66	-0,40	b*Av	23,85	23,47	-0,38	0,59	
	Inhibitor I												
L*1	12,85	15,26	2,41	a*1	43,7	46,56	2,86	b*1	22,15	26,29	4,14	5,58	*0,17*
L*2	12,64	15,19	2,55	a*2	43,42	46,46	3,04	b*2	21,79	26,17	4,38	5,91	
L*3	12,58	15,06	2,48	a*3	43,33	46,31	2,98	b*3	21,67	25,95	4,28	5,77	
L*Av	12,69	15,17	2,48	a*Av	43,48	46,44	2,96	b*Av	21,87	26,14	4,27	5,75	

C.6.5 Colourimetric measurements of Cochineal dyed samples exposed for 100h at 35°C, 50%RH

	before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	*Standard deviation*
	Blank												
L*1	15,22	16,19	0,97	a*1	46,91	47,82	0,91	b*1	26,24	27,9	1,66	2,13	*0,45*
L*2	14,82	16,09	1,27	a*2	46,47	47,69	1,22	b*2	25,54	27,72	2,18	2,80	
L*3	14,59	15,94	1,35	a*3	46,18	47,48	1,3	b*3	25,14	27,47	2,33	2,99	
L*Av	14,88	16,07	1,20	a*Av	46,52	47,66	1,14	b*Av	25,64	27,70	2,06	2,64	
	Inhibitor A												
L*1	12,63	15,81	3,18	a*1	43,76	47,42	3,66	b*1	21,77	27,25	5,48	7,32	*0,23*
L*2	12,59	15,65	3,06	a*2	43,7	47,24	3,54	b*2	21,7	26,97	5,27	7,05	
L*3	12,62	15,6	2,98	a*3	43,75	47,17	3,42	b*3	21,74	26,89	5,15	6,86	
L*Av	12,61	15,69	3,07	a*Av	43,74	47,28	3,54	b*Av	21,74	27,04	5,3	7,08	
	Inhibitor B												
L*1	12,41	16,3	3,89	a*1	43,16	47,88	4,72	b*1	21,39	28,1	6,71	9,08	*0,59*
L*2	11,89	15,91	4,02	a*2	42,51	47,41	4,9	b*2	20,48	27,42	6,94	9,40	
L*3	12,38	15,92	3,54	a*3	43,16	47,43	4,27	b*3	21,33	27,44	6,11	8,25	
L*Av	12,23	16,04	3,82	a*Av	42,94	47,57	4,63	b*Av	21,07	27,65	6,59	8,91	
	Inhibitor C												
L*1	12,19	15,09	2,9	a*1	43,08	46,47	3,39	b*1	21	26	5	6,70	*1,61*
L*2	11,47	15,26	3,79	a*2	42,14	46,66	4,52	b*2	19,76	26,29	6,53	8,80	
L*3	10,95	15,17	4,22	a*3	41,41	46,57	5,16	b*3	18,87	26,14	7,27	9,86	
L*Av	11,54	15,17	3,64	a*Av	42,21	46,57	4,36	b*Av	19,88	26,14	6,27	8,45	
	Inhibitor D												
L*1	12,23	15,82	3,59	a*1	43,37	47,32	3,95	b*1	21,07	27,27	6,2	8,18	*0,36*
L*2	12,17	16,01	3,84	a*2	43,3	47,54	4,24	b*2	20,98	27,59	6,61	8,74	
L*3	12,22	16,11	3,89	a*3	43,35	47,65	4,3	b*3	21,06	27,76	6,7	8,86	
L*Av	12,21	15,98	3,77	a*Av	43,34	47,50	4,16	b*Av	21,04	27,54	6,50	8,59	

	before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	*Standard deviation*
	Inhibitor E												
L*1	10,98	14,51	3,53	a*1	41,91	45,74	3,83	b*1	18,93	25	6,07	8,00	*0,41*
L*2	11,09	14,44	3,35	a*2	42,03	45,7	3,67	b*2	19,1	24,89	5,79	7,63	
L*3	11,47	14,66	3,19	a*3	42,55	45,92	3,37	b*3	19,77	25,26	5,49	7,19	
L*Av	11,18	14,54	3,36	a*Av	42,16	45,79	3,62	b*Av	19,27	25,05	5,78	7,61	
	Inhibitor F												
L*1	12,32	15,07	2,75	a*1	43,4	46,43	3,03	b*1	21,22	25,96	4,74	6,26	*1,59*
L*2	12,68	14,56	1,88	a*2	43,79	45,84	2,05	b*2	21,86	25,09	3,23	4,26	
L*3	13,02	14,4	1,38	a*3	44,17	45,67	1,5	b*3	22,44	24,81	2,37	3,13	
L*Av	12,67	14,68	2,00	a*Av	43,79	45,98	2,19	b*Av	21,84	25,29	3,45	4,55	
	Inhibitor G												
L*1	14,76	15,34	0,58	a*1	46,22	46,79	0,57	b*1	25,43	26,44	1,01	1,30	*0,22*
L*2	14,69	15,39	0,7	a*2	46,18	46,84	0,66	b*2	25,32	26,52	1,2	1,54	
L*3	14,82	15,32	0,5	a*3	46,32	46,75	0,43	b*3	25,54	26,41	0,87	1,09	
L*Av	14,76	15,35	0,59	a*Av	46,24	46,79	0,55	b*Av	25,43	26,46	1,03	1,31	
	Inhibitor H												
L*1	14,2	13,45	-0,75	a*1	45,49	44,53	-0,96	b*1	24,46	23,18	-1,28	1,77	*0,73*
L*2	13,72	13,47	-0,25	a*2	44,92	44,57	-0,35	b*2	23,65	23,22	-0,43	0,61	
L*3	13,6	13,43	-0,17	a*3	44,75	44,5	-0,25	b*3	23,43	23,14	-0,29	0,42	
L*Av	13,84	13,45	-0,39	a*Av	45,05	44,53	-0,52	b*Av	23,85	23,18	-0,67	0,93	
	Inhibitor I												
L*1	12,85	16,5	3,65	a*1	43,7	48,04	4,34	b*1	22,15	28,43	6,28	8,46	*0,62*
L*2	12,64	16,71	4,07	a*2	43,42	48,3	4,88	b*2	21,79	28,8	7,01	9,46	
L*3	12,58	16,7	4,12	a*3	43,33	48,27	4,94	b*3	21,67	28,78	7,11	9,59	
L*Av	12,69	16,64	3,95	a*Av	43,48	48,20	4,72	b*Av	21,87	28,67	6,8	9,17	

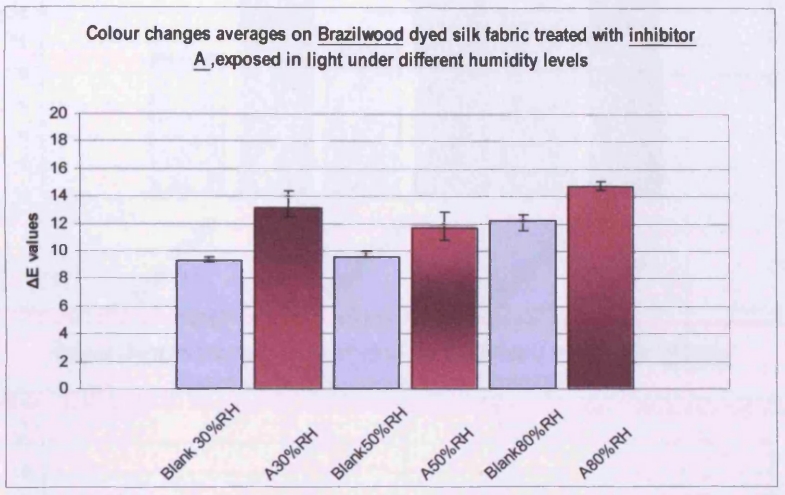
C.6.6 Colourimetric measurements of Cochineal dyed samples exposed for 100h at 35°C, 80%RH

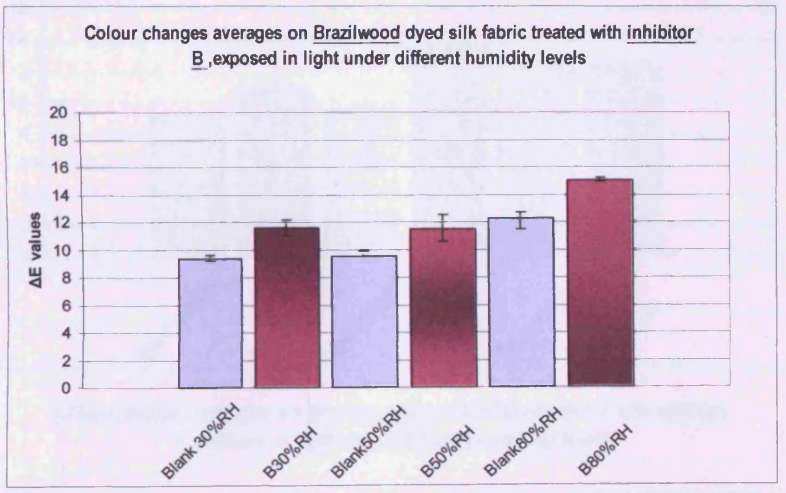
	before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	*Standard deviation*
	Blank sample												
L*1	15,22	16,75	1,53	a*1	46,91	47,78	0,87	b*1	26,24	28,57	2,33	2,92	
L*2	14,82	16,49	1,67	a*2	46,47	47,52	1,05	b*2	25,54	28,41	2,87	3,48	
L*3	14,59	16,59	2	a*3	46,18	47,7	1,52	b*3	25,14	28,58	3,44	4,26	
L*Av	14,88	16,61	1,73	a*Av	46,52	47,67	1,15	b*Av	25,64	28,52	2,88	3,55	*0,55*
	Inhibitor A												
L*1	12,63	20,04	7,41	a*1	43,76	51,21	7,45	b*1	21,77	34,54	12,77	16,54	
L*2	12,59	20,32	7,73	a*2	43,7	51,38	7,68	b*2	21,7	35,01	13,31	17,20	
L*3	12,62	20,13	7,51	a*3	43,75	51,23	7,48	b*3	21,74	34,69	12,95	16,73	
L*Av	12,61	20,16	7,55	a*Av	43,74	51,27	7,54	b*Av	21,74	34,75	13,01	16,82	*0,28*
	Inhibitor B												
L*1	12,41	15,9	3,49	a*1	43,16	47,29	4,13	b*1	21,39	27,41	6,02	8,09	
L*2	11,89	16,65	4,76	a*2	42,51	48	5,49	b*2	20,48	28,69	8,21	10,96	
L*3	12,38	16,73	4,35	a*3	43,16	48,08	4,92	b*3	21,33	28,84	7,51	9,98	
L*Av	12,23	16,43	4,20	a*Av	42,94	47,79	4,85	b*Av	21,07	28,31	7,25	9,68	*1,19*
	Inhibitor C												
L*1	12,19	19,57	7,38	a*1	43,08	50,74	7,66	b*1	21	33,73	12,73	16,59	
L*2	11,47	19,45	7,98	a*2	42,14	50,64	8,5	b*2	19,76	33,53	13,77	18,04	
L*3	10,95	19,56	8,61	a*3	41,41	50,74	9,33	b*3	18,87	33,7	14,83	19,52	
L*Av	11,54	19,53	7,99	a*Av	42,21	50,71	8,50	b*Av	19,88	33,65	13,78	18,05	*1,20*
	Inhibitor D												
L*1	12,23	18,17	5,94	a*1	43,37	49,45	6,08	b*1	21,07	31,32	10,25	13,32	
L*2	12,17	18,21	6,04	a*2	43,3	49,46	6,16	b*2	20,98	31,39	10,41	13,52	
L*3	12,22	18,07	5,85	a*3	43,35	49,36	6,01	b*3	21,06	31,15	10,09	13,12	
L*Av	12,21	18,15	5,94	a*Av	43,34	49,42	6,08	b*Av	21,04	31,29	10,25	13,32	*0,16*

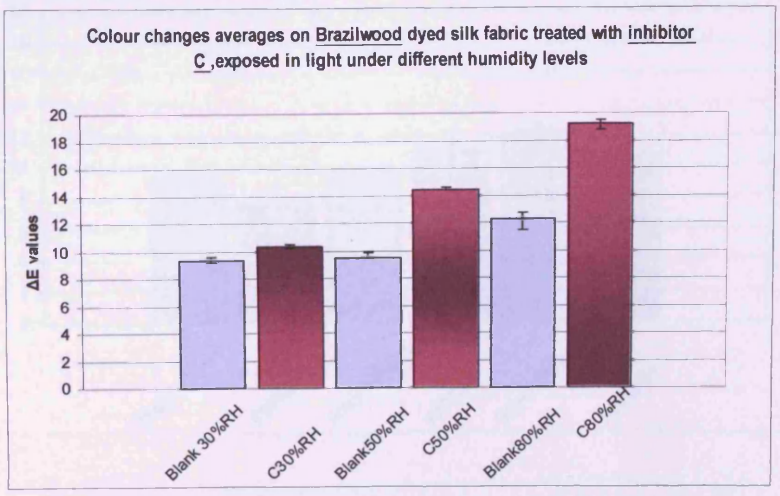
	before	after	ΔL*		before	after	Δa*		before	after	Δb*	ΔE	*Standard deviation*
	Inhibitor E												
L*1	10,98	15,71	4,73	a*1	41,91	46,93	5,02	b*1	18,93	27,07	8,14	10,67	
L*2	11,09	15,69	4,6	a*2	42,03	46,93	4,9	b*2	19,1	27,03	7,93	10,39	
L*3	11,47	15,81	4,34	a*3	42,55	47,09	4,54	b*3	19,77	27,25	7,48	9,77	
L*Av	11,18	15,74	4,56	a*Av	42,16	46,98	4,82	b*Av	19,27	27,12	7,85	10,28	*0,38*
	Inhibitor F												
L*1	12,32	15,8	3,48	a*1	43,4	47,15	3,75	b*1	21,22	27,24	6,02	7,90	
L*2	12,68	15,77	3,09	a*2	43,79	47,09	3,3	b*2	21,86	27,17	5,31	6,97	
L*3	13,02	15,8	2,78	a*3	44,17	47,16	2,99	b*3	22,44	27,24	4,8	6,30	
L*Av	12,67	15,79	3,12	a*Av	43,79	47,13	3,35	b*Av	21,84	27,22	5,38	7,06	*0,66*
	Inhibitor G												
L*1	14,76	16,77	2,01	a*1	46,22	47,64	1,42	b*1	25,43	28,9	3,47	4,25	
L*2	14,69	16,71	2,02	a*2	46,18	47,58	1,4	b*2	25,32	28,8	3,48	4,26	
L*3	14,82	16,3	1,48	a*3	46,32	47,1	0,78	b*3	25,54	28,1	2,56	3,06	
L*Av	14,76	16,59	1,84	a*Av	46,24	47,44	1,2	b*Av	25,43	28,6	3,17	3,86	*0,57*
	Inhibitor H												
L*1	14,2	15,75	1,55	a*1	45,49	47,1	1,61	b*1	24,46	27,15	2,69	3,50	
L*2	13,72	15,71	1,99	a*2	44,92	47,01	2,09	b*2	23,65	27,07	3,42	4,47	
L*3	13,6	15,93	2,33	a*3	44,75	47,3	2,55	b*3	23,43	27,44	4,01	5,29	
L*Av	13,84	15,80	1,96	a*Av	45,05	47,14	2,08	b*Av	23,85	27,22	3,37	4,42	*0,73*
	Inhibitor I												
L*1	12,85	19,03	6,18	a*1	43,7	50,21	6,51	b*1	22,15	32,8	10,65	13,93	
L*2	12,64	19,07	6,43	a*2	43,42	50,21	6,79	b*2	21,79	32,86	11,07	14,49	
L*3	12,58	18,98	6,4	a*3	43,33	50,16	6,83	b*3	21,67	32,71	11,04	14,47	
L*Av	12,69	19,03	6,34	a*Av	43,48	50,19	6,71	b*Av	21,87	32,79	10,92	14,30	*0,26*

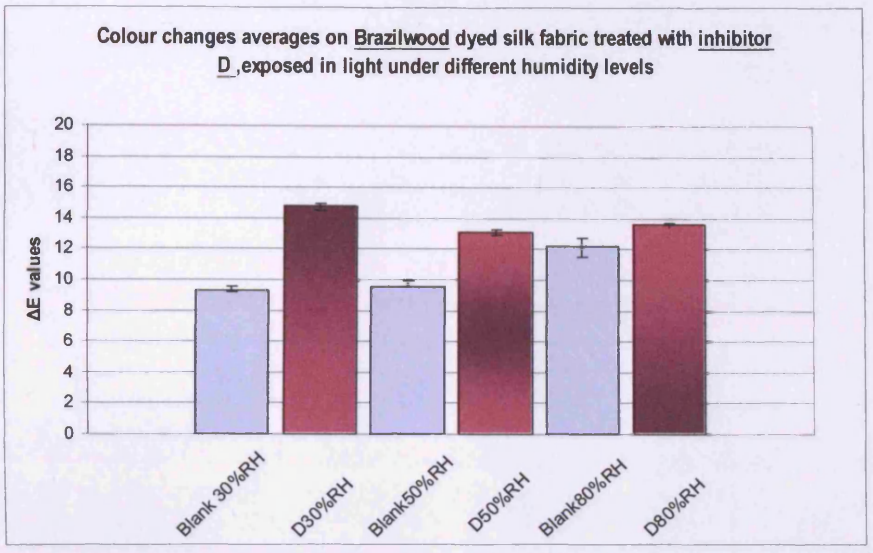
C.7 Colour changes on samples exposed at different humidity levels

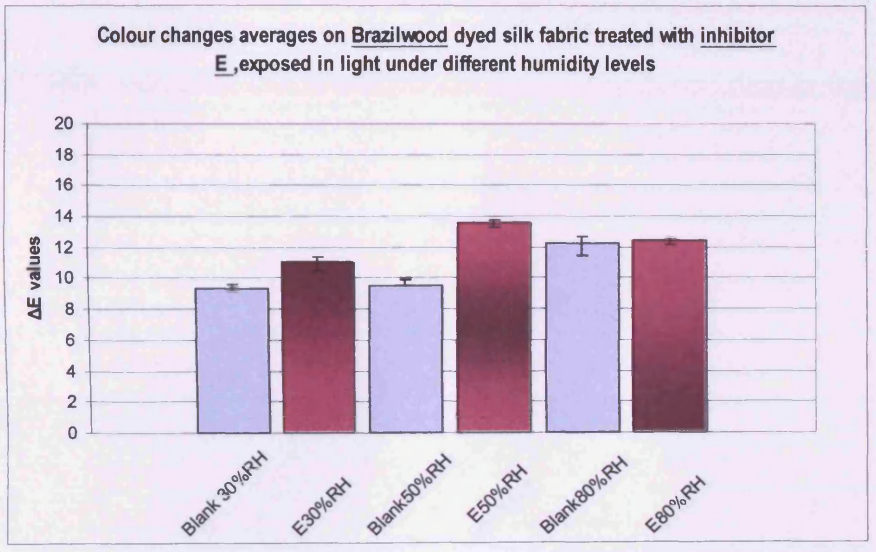
C.7.1 Colour changes on Brazilwood dyed samples

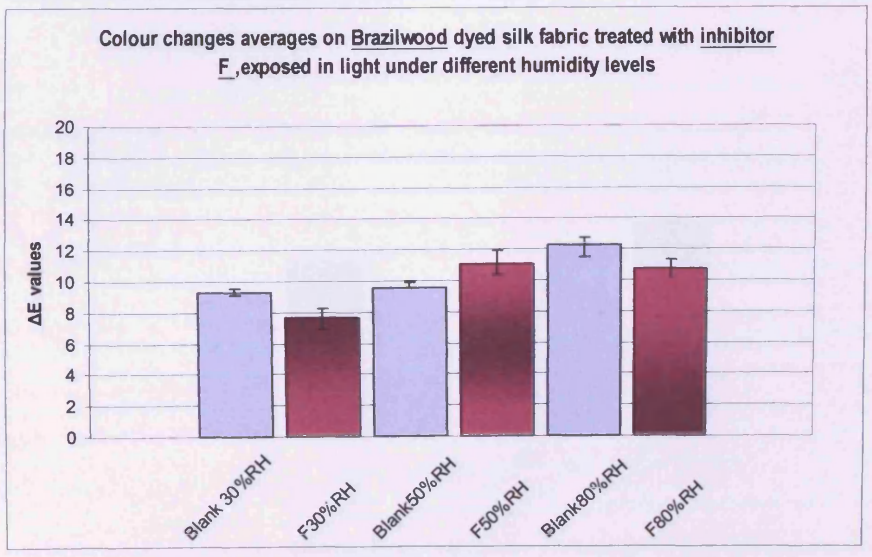


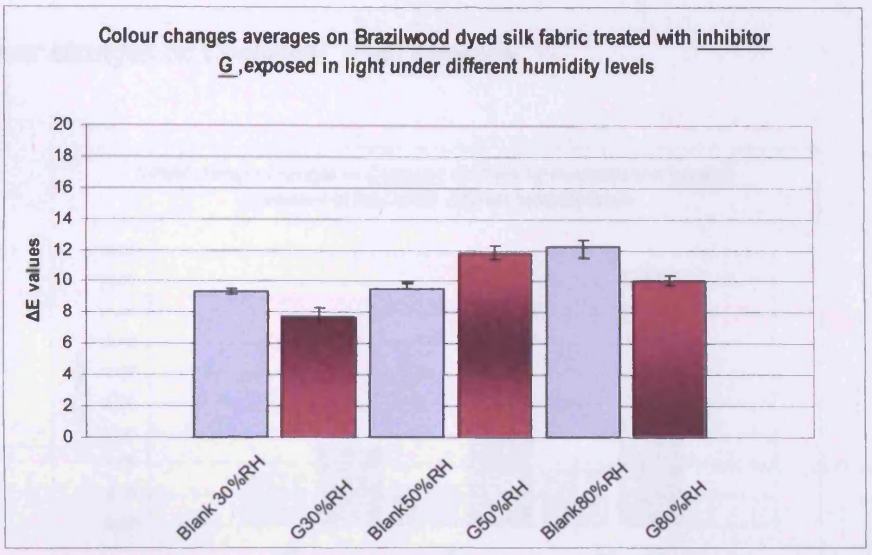


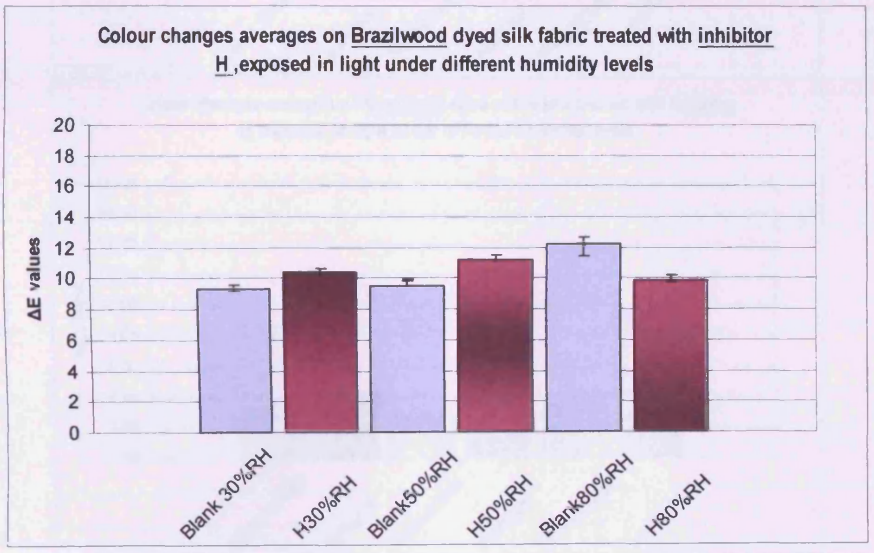


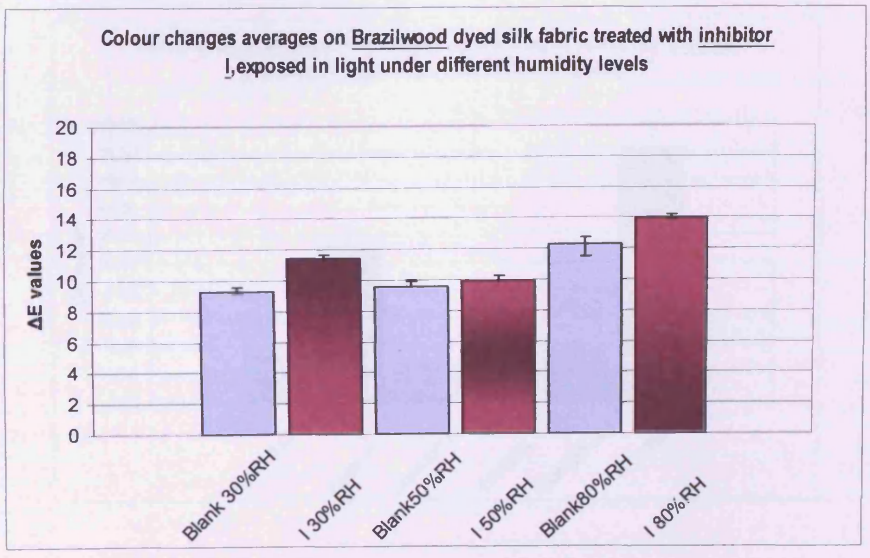

Colour changes averages on Brazilwood dyed silk fabric treated with inhibitor D ,exposed in light under different humidity levels
ΔE values
20
18
16
14
12
10
8
6
4
2
0
Blank 30%RH
D30%RH
Blank50%RH
D50%RH
Blank80%RH
D80%RH


Colour changes averages on Brazilwood dyed silk fabric treated with inhibitor E ,exposed in light under different humidity levels
ΔE values
20
18
16
14
12
10
8
6
4
2
0
Blank 30%RH
E30%RH
Blank50%RH
E50%RH
Blank80%RH
E80%RH

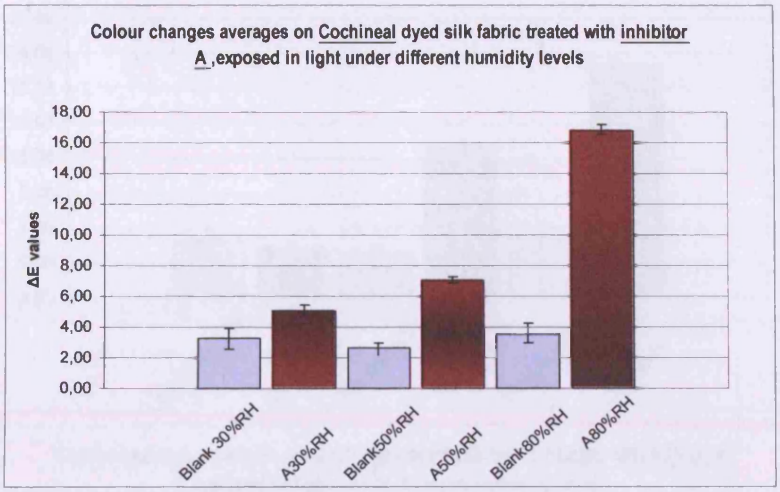

Colour changes averages on Brazilwood dyed silk fabric treated with inhibitor F ,exposed in light under different humidity levels
ΔE values
20
18
16
14
12
10
8
6
4
2
0
Blank 30%RH
F30%RH
Blank50%RH
F50%RH
Blank80%RH
F80%RH

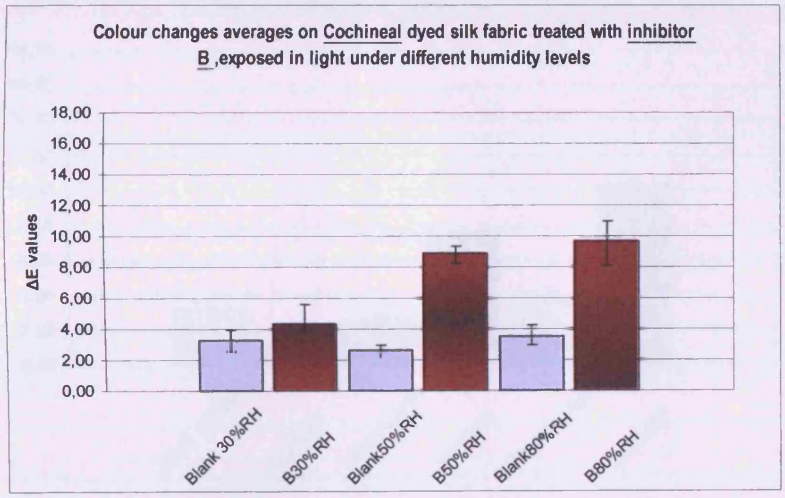

Colour changes averages on Brazilwood dyed silk fabric treated with inhibitor G ,exposed in light under different humidity levels
ΔE values
20
18
16
14
12
10
8
6
4
2
0
Blank 30%RH
G30%RH
Blank50%RH
G50%RH
Blank80%RH
G80%RH

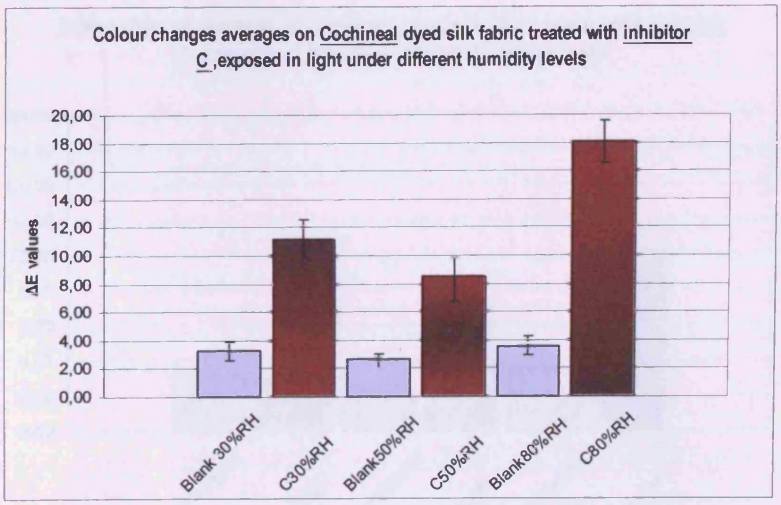

Colour changes averages on Brazilwood dyed silk fabric treated with inhibitor H ,exposed in light under different humidity levels
ΔE values
20
18
16
14
12
10
8
6
4
2
0
Blank 30%RH
H30%RH
Blank50%RH
H50%RH
Blank80%RH
H80%RH

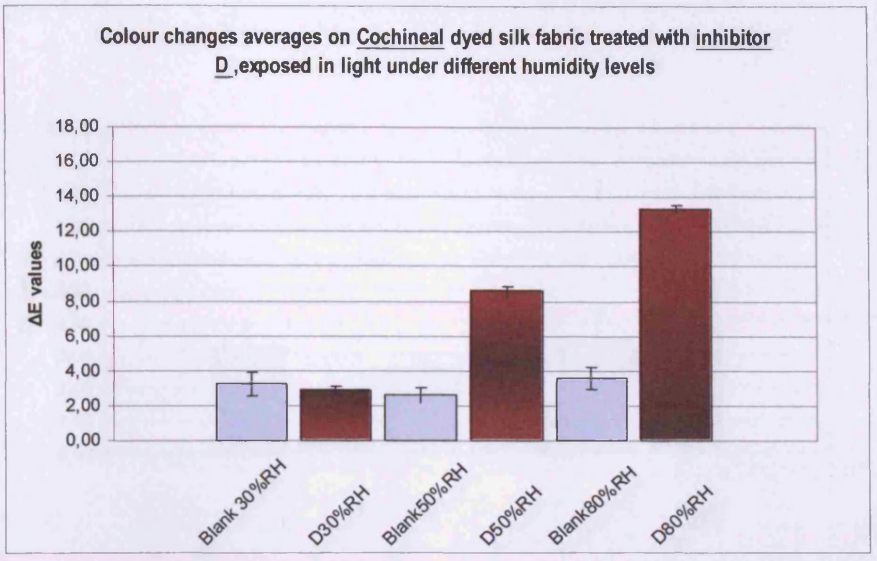

Colour changes averages on Brazilwood dyed silk fabric treated with inhibitor I,exposed in light under different humidity levels
ΔE values
20
18
16
14
12
10
8
6
4
2
0
Blank 30%RH
I 30%RH
Blank50%RH
I 50%RH
Blank80%RH
I 80%RH

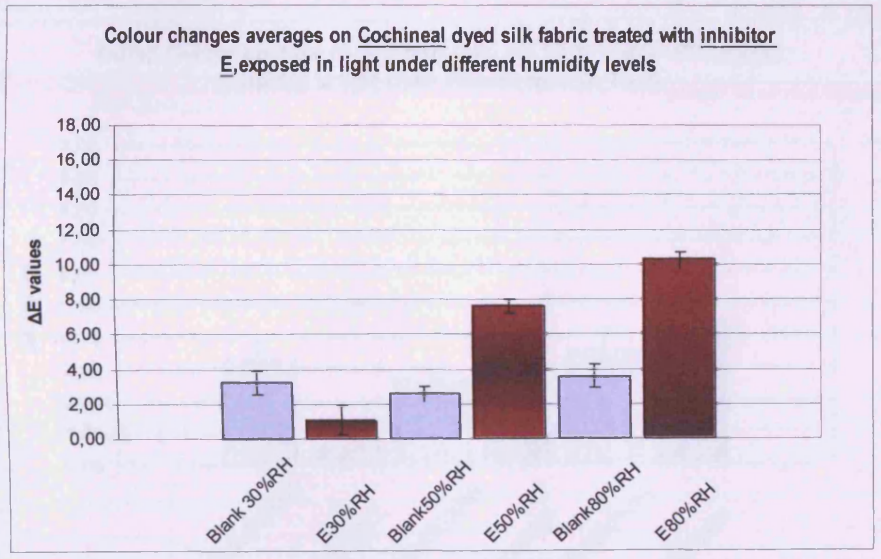
C.7.2 Colour changes on Cochineal dyed samples

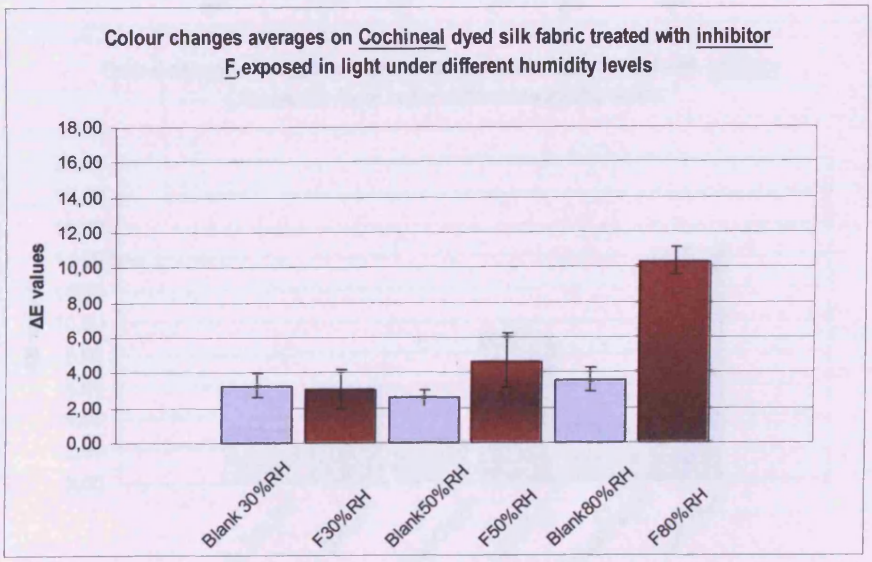


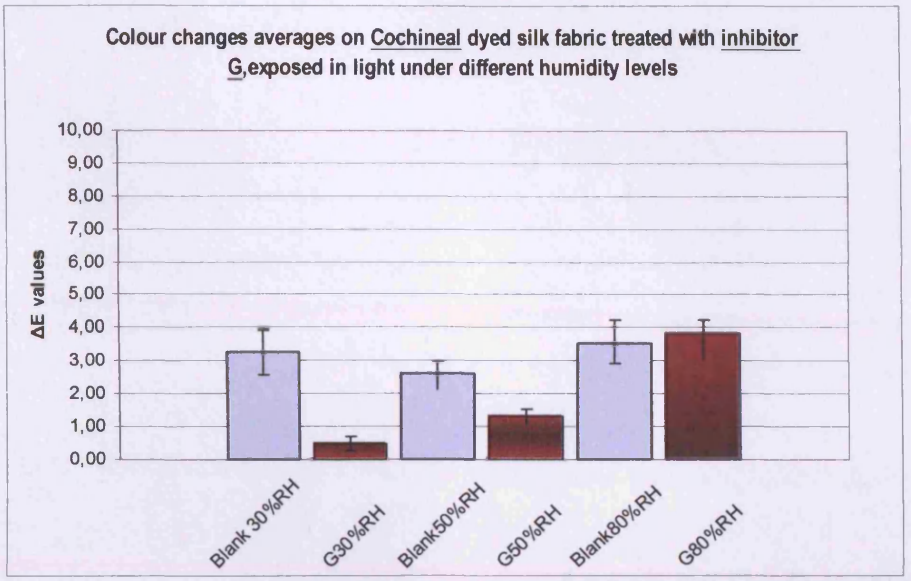


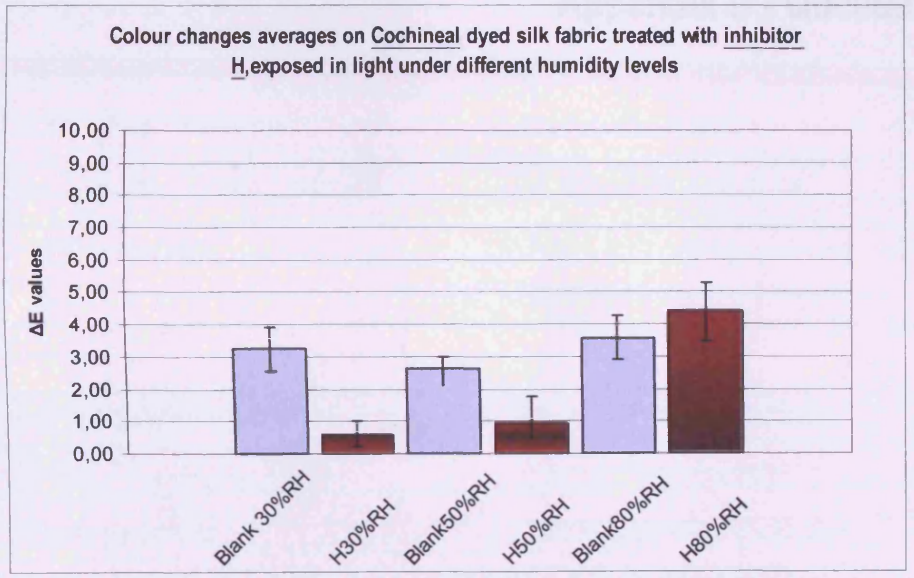


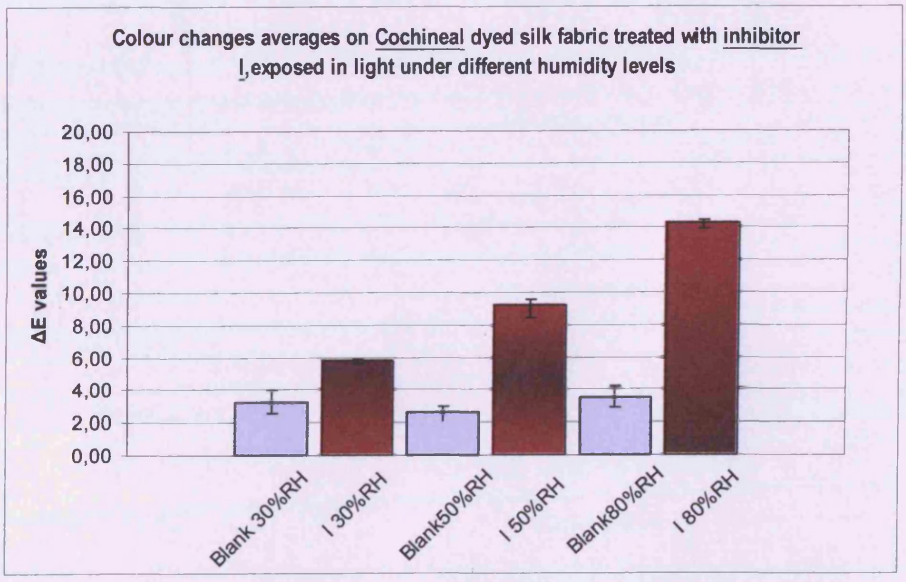

Colour changes averages on Cochineal dyed silk fabric treated with inhibitor D ,exposed in light under different humidity levels
ΔE values
18,00
16,00
14,00
12,00
10,00
8,00
6,00
4,00
2,00
0,00
Blank 30%RH
D30%RH
Blank50%RH
D50%RH
Blank80%RH
D80%RH


Colour changes averages on Cochineal dyed silk fabric treated with inhibitor E,exposed in light under different humidity levels
ΔE values
18,00
16,00
14,00
12,00
10,00
8,00
6,00
4,00
2,00
0,00
Blank 30%RH
E30%RH
Blank50%RH
E50%RH
Blank80%RH
E80%RH


Colour changes averages on Cochineal dyed silk fabric treated with inhibitor F,exposed in light under different humidity levels
ΔE values
18,00
16,00
14,00
12,00
10,00
8,00
6,00
4,00
2,00
0,00
Blank 30%RH
F30%RH
Blank50%RH
F50%RH
Blank80%RH
F80%RH


Colour changes averages on Cochineal dyed silk fabric treated with inhibitor G,exposed in light under different humidity levels
ΔE values
10,00
9,00
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
Blank 30%RH
G30%RH
Blank50%RH
G50%RH
Blank80%RH
G80%RH


Colour changes averages on Cochineal dyed silk fabric treated with inhibitor H,exposed in light under different humidity levels
ΔE values
10,00
9,00
8,00
7,00
6,00
5,00
4,00
3,00
2,00
1,00
0,00
Blank 30%RH
H30%RH
Blank50%RH
H50%RH
Blank80%RH
H80%RH


Colour changes averages on Cochineal dyed silk fabric treated with inhibitor I,exposed in light under different humidity levels
ΔE values
20,00
18,00
16,00
14,00
12,00
10,00
8,00
6,00
4,00
2,00
0,00
Blank 30%RH
I 30%RH
Blank50%RH
I 50%RH
Blank80%RH
I 80%RH

Appendix D - Questionnaires

D.1 People responded in the questionnaires

	Responsibility	Museum/ workshop
1	Textile Conservator	-
2	Head of studies and research	The Textile Conservation Centre
3	Head of organics	National Museums and Galleries on Merseyside. The Conservation Centre.
4	Director	Manchester Ancient Textile Unit
5	Keeper of costume and textiles	Museum of Costume and Textiles, Nottingham.
6	Textile Conservator	Scottish Museum Council
7	Textile conservator	Byzantine Museum of Athens
8	Senior textile conservator	Museum of London
9	Head of studio. Textile conservation	Victoria and Albert Museum
10	Textile conservator	Cultural and Leisure Services. The Burrell Collection. Glasgow City Council.
11	Partner	-
12	Freelance textile conservator	The Textile Restoration Studio
13	Keeper, Costume and Textiles	Tyne and Wear Museums
14	Keeper of costume	Gallery of Costume, Manchester.
15	Textile conservator	Museum of Folk Art, Athens
16	Conservator	The National Trust
17	Textile conservator	Benaki Museum
18	Head of organic artefacts conservation section	The British Museum
19	Textile conservator	Benaki Museum
20	Assistant keeper of arts	-
21	Textile conservation officer	Museum of Welsh Life and National Museums and Galleries of Wales
22	Keeper of costume and textiles	Luton Museum

D.2 1st Questionnaire

UCL
Institute of Archaeology

Research on Photodegradation of Textiles

I am a research student in the Institute of Archaeology , UCL and my research area is the deterioration of natural dyed historic textiles of 16th-19th century, caused by exposure to light. Apart from the study of photodegradation, I am very interested to introduce new and easy methods of protection and conservation for these textile materials. It would be therefore; very useful to use your experience in museum textiles so as to investigate the problems you are facing in their care and conservation. I would be grateful if you complete the following questionnaire and return it to me, no later than 15 September 1997. Please pass this questionnaire to any other person you know, who also works with museum textiles and is willing to help.

Tatiana Koussoulou

e-mail:

Note: where there are boxes, please tick more than one if you like.

1. Name of person completing this questionnaire and responsibility:

_____

_____

2. What is the nature of the textile collection in your Museum?

_____

_____

3. What type of deterioration have you observed on textiles in display, in the collections you are working with?

Mechanical damage ☐ Chemical damage ☐

Fading by light ☐ Other _____

4. Are there any dyed textiles which seem to be faded by sunlight (or light in general)

_____

_____

5. What is the usual change observed on a photo-degraded textile object in your collections?

Color: _____

Texture: _____

Strength: _____

6. Do you know if these objects are made from fibres of natural origin? And if yes, which ones?

Wool ☐ Silk ☐ Cotton ☐ Linen ☐

_____

7. Do you know if they are dyed with natural dyes? If yes, do you know which type of natural dyes were used?

Vegetable ☐ Animal (insect) ☐

Others: _____

8. What type of natural textile material do you find most vulnerable to photodegradation, according to your experience in your collections?

Wool ☐ Silk ☐ Cotton ☐ Linen ☐

_____

9. Do you think, any particular natural dye is more vulnerable to light than the others?

_____

_____

10. Which colour on textiles, do you find most vulnerable to photodegradation, according to your experience in your collections?

Red ☐ Blue ☐ Yellow ☐ Purple ☐ Green ☐

Other _____

11. - Which combination of textile material and color do you find most vulnerable?

_____

_____

12. Do you think that the mixtures of different materials on the same object make it more susceptible to photodegradation, according to your experience in your collections? If yes, which combinations are more light sensitive?

Mixtures of different dyes ☐ Mixtures of different fibres ☐

Mixtures of organic and inorganic materials on the same object (textile fibres ,metals, pigments, stones e.t.c) ☐ Mixtures of organic materials (textile fibres , paper, leather, other, e.t.c) ☐

Other comments:_____

13. Have you noticed if the photo-deteriorated textiles come from particular periods or areas? If yes, from which area or period?

_____

_____

14. Is there anything special or different about the construction material of deteriorated objects?

Nature of fibres ☐ Nature of dyes ☐ Construction techniques ☐

Usual treatments ☐ Other: _____

_____

15. - Do you know the conditions these textiles were kept (used and stored) before they came into the museum?

_____

_____

16. Do you know if these objects came into the museum already photo-deteriorated?

Yes ☐ No ☐

17. Do you believe they became subject to photodegradation in the museum because of the lighting conditions in the display?

Yes ☐ No ☐

18 - Do you know the way they were usually cleaned or washed (or treated) before they came into the Museum?

_____

_____

19. - Do you know the conditions under which these textiles were displayed or stored in the museum before their present display? If yes, for how long they were exposed to non controlled lighting conditions and in which way?

_____

Near open windows ☐ Open display ☐ Displays cases ☐

Other: _____

20.-What was/is the support material used for their display?

_____

_____

21. Do you know the environmental conditions on display in your museum? If yes, do you believe they are responsible for light degradation of your textile objects?

Yes ☐ No ☐

_____

22. Which environmental factor do you believe is exaggerating the light degradation of the textiles in your collection?

High Humidity ☐ Low Humidity ☐ Air Pollution ☐

High Temperature ☐ Low Temperature ☐ No relation ☐

23. Was photodegradation made you change the way your textiles are stored and displayed?

_____

24. How textiles are displayed in your Museum now and what protection methods (protection from light) do you use for them?

Keep in the dark ☐ Special cases with UV filters ☐

Controlled artificial light ☐ Other: _____

_____

25. What type of artificial lighting is used in your display?

_____

_____

26. Do you know any kind of finishing after dyeing , which seems to interfere with the light fastness of the textile material or the dye used?

_____

27. Please add any comments:

Thank you for completing this questionnaire, your answers will be most helpful.

D.3 2nd Questionnaire

Institute of Archaeology
University College London

Research in the Photostabilization of Museum Textiles

Dear Sir/Madam,

I am a Ph.D. student in the Institute of Archaeology, UCL. My research is focused on the study of light deterioration of historic textiles in the museum environment and their photostabilization. During my three-year study, I am testing the effectiveness and suitability of photostabilizing materials, also known as light stabilizers, for use in textile conservation. I will be therefore most interested to include in my final thesis, the opinion and experience of people working in the textile conservation field, on the introduction of these new materials as a conservation procedure. I would be most grateful if you would complete the following questionnaire and return it to me, no later than 30 July 1999. Please pass this questionnaire to any other person you know, who also works with museum textiles and is willing to help.

Tatiana Koussoulou

Note: where there are boxes, please tick as many boxes as are applicable

1. Name of the person completing this questionnaire and responsibility:

2. **Which methods of protection from photodegradation of textile materials are at present in use in your museum/collection?**

❑ UV filters on windows	20[31]
❑ Display cases with UV filters	15
❑ Exclusion/control of natural light	20
❑ Controlled artificial lighting	22
❑ Lighting activated by the visitors	2
❑ Storage in darkness	22
❑ None	
❑ Other (please specify):	2

3. **Are you happy with the preventive conservation methods in your museum/collection from light deterioration? Do you find them sufficient?**

❑ YES	12
❑ NO	13

4. **Do you think that an additional/alternative method of protection in the form of treatment on the object itself would be a good idea?**

❑ YES	10
❑ NO	10
❑ MAYBE	3

5. **Light stabilizers are materials which are applied on the textile fibres with solvent solutions and are absorbed by them. They do not affect the colour of the textile and the effect on texture after drying is hardly noticeable. Tests so far have demonstrated that the light fastness (protection from fading) of dyed textiles is increased over 50%, in some cases. Will you be willing to use them as a final conservation treatment?**

❑ YES	7
❑ NO	10
❑ MAYBE	4

[31] Number on the right show the number of people selected this answer

6. **Light stabilizers are polymeric materials used in recent years on polymers, synthetic and natural fibres in the modern textile industry, in order to improve the light fastness of plastics and synthetic textiles. They have also been tested for use in painting conservation. They have been added to varnishes for the protection of coloured pigments. How do you feel about using them in textile conservation?**

- ❑ I would use them. I like the idea.
- ❑ I would use them only if there is no other available method of protection from light deterioration. 12
- ❑ I would use them only on very light sensitive materials, where other methods are not sufficient . 6
- ❑ I would never use a material like that. 8

Could you please say why you wouldn't use them: _____

_____

_____

7. **Light stabilizers are only soluble in organic solvents and can be combined with the dry cleaning procedure of textiles, where a small quantity of stabilizer (2%) can be added to the bath. They can also be applied by spraying the surface in the case of a very fragile textile. The solvent used so far, for experimental work is Tetrachloroethylene (also known as Perchloroethylene, Perclene). Do you find the above methods of application acceptable?**

- ❑ YES 8
- ❑ NO 15

Comments: _____

_____

8. **If no, for which reason?**

- ❑ Method of application too difficult. 7
- ❑ Need of special equipment, which is not available. 15
- ❑ Health hazards associated with the solvent. 15
- ❑ Other (please specify): 7

9. Although reversibility of light stabilizers is still under evaluation, it is noticed that almost 90% of the materials can be removed from the textile, if this is desirable, by immersion in the same solvent. Do you think this satisfies conservation requirements?

- ❑ Yes, it is acceptable.
- ❑ I do not like it, but I would use light stabilizers anyway.
- ❑ I do not like it, but I would use them if there is no other method of protection. 7
- ❑ I will not use light stabilizers unless I am 100% sure I can remove them from the textile.18

10. Please give any other comments you think will be useful for my research:

Thank you for completing this questionnaire, your answers will be most helpful